Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 196 JULY, 1923 No. 1

THE ELECTRON IN CHEMISTRY.*†

BY

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THE MECHANISM OF CHEMICAL COMBINATION.

Let us in the first place consider chemical combinations between gases. That something more than collisions between the molecules of the reacting gases is required is clear, from the fact that gases like hydrogen and oxygen, hydrogen and chlorine (in the dark), which can form very stable compounds, can be mixed without any appreciable amount of chemical combination taking place at moderate temperatures. The test is a very severe one since at atmospheric pressure each molecule of oxygen in a mixture of hydrogen and oxygen would in one second collide with many million hydrogen molecules, so that even if only one collision in a million were to result in combination the rate of combination would be very great. A mixture of hydrogen and oxygen in the proportion of two molecules of hydrogen to one of oxygen can be stable, (*a*) when the gases are uncombined, and (*b*) when they are combined and the mixture exists as water vapour. The large evolution of heat observed in the transit from (*a*) to (*b*) shows that (*b*) has much less potential energy than (*a*). The fact that the gases can exist side by side without combination shows that

* A series of lectures given before The Franklin Institute, April 9–13, 1923.

† Continued from the June, 1923, issue, p. 785.

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the phase of high potential energy does not spontaneously pass to one of lower. We have many examples of this in ordinary mechanics. Thus the water in a mountain lake has more potential energy than it would have if it ran down into the valley, it does not do so because before it could get away work would have to be supplied to raise it above the level of the height immediately surrounding it. If a syphon is put into the lake this work is forthcoming and the water will run out. To enable a system to pass to a state of smaller potential energy may require the expenditure of a certain amount of energy and if this is not forthcoming the change will not take place. Thus, if a preliminary to the combination of hydrogen and oxygen were the dissociation of the molecules of these gases into atoms, the gases would not combine unless the very considerable amount of energy required for this initial stage were available. Now in the mixture of two pure gases the energy available is that due to the thermal agitation of the molecule; this at 0° C. is only about 1/30 of a volt per molecule, and is small compared with the changes in energy occurring in chemical processes which on the same scale would be represented by several volts. Thus we might expect that unless some source of energy besides that due to thermal agitation were available, the combination would not take place. In the case we have just been considering, that of the dissociation of electrolytes in solution, the main part of the energy required to separate the ions in the electrolyte came not from thermal agitation, but from that derived from the falling in of polar molecules, *i.e.*, from the energy of chemical separation of the polar molecule and the molecule of the electrolyte.

The effect of water vapour, whose molecule is strongly polar, on the combination of gases is well known. Thus, H. B. Baker showed that very carefully dried HCl and NH_3 would not combine, that the combination of H_2 and Cl_2 went on exceedingly slowly, even in strong sunlight, when the gases were carefully dried, while H. B. Dixon showed that electric sparks might be passed through a mixture of dry CO and O_2 without combination taking place. He also showed that other substances besides water vapour render possible the combination between CO and O, and it is probable that all polar molecules possess this property to a greater or less extent. Baker found that the effect of water vapour was not confined to combination if extended also to dis-

sociation, for while ordinary ammonium chloride is dissociated to a very considerable extent when the temperature is raised to three or four hundred degrees centigrade, no dissociation occurs at these temperatures if the salt is very carefully dried.

When polar molecules, such as those of water or ammonia, are present, they may combine with the other molecules, forming aggregates in which, as in the case discussed in a previous lecture, there is a kind of incipient ionization, the atoms being more widely separated than in the normal molecule. The aggregate has a finite electrical moment and thus exerts much greater forces on neighbouring molecules than the normal molecule. Let us represent these aggregates by $A(H_2O)_n$, $B(H_2O)_m$ when A and B represent molecules of the reacting gases. When two of these come together the work required to separate them may be so much greater than that required to separate AB that though A and B cannot by collision form a potent aggregate $A(H_2O)_n$ and $B(H_2O)_m$ are able to do so. After the aggregate has been formed the atoms, loosened by the action of the polar molecules, rearrange themselves so as to produce the system with the minimum potential energy. If, as the result of this rearrangement, the water is set free, it will be available for producing a further supply of the complex molecules. Even if only a small percentage of the molecules are in the complex state the rate of combination might be considerable, as the number of collisions made by a molecule under ordinary circumstances is so large. Thus to take the combination of gaseous HCl and NH_3 to form NH_4Cl as an example. If even only one molecule in a hundred thousand were in the complex state and if the combination only occurs when a complex molecule of HCl collides with a complex one of NH_3, these collisions will still be so numerous that something like one per cent. of the HCl and NH_3 will combine per second. We see from this that to avoid appreciable combination the gases must be exceedingly dry, and that traces of water too small to be detected by other means might produce very marked effects on chemical combination.

On this view of chemical combination the rearrangement of the atoms takes place inside a complex formed with the polar molecules, thus no ions need get free. There is very strong evidence against the necessity for the existence of free ions in gaseous combinations; free ions make a gas a conductor of electricity and the conductivity due to free ions can be detected when the number

of free ions is much less than one-million-millionth of the number of molecules. Many cases of chemical combination have been tested for electrical conductivity without any trace of it being detected. Thus L. Bloch [18] showed that many chemical actions which go on at moderate temperatures, such as the oxidation of nitric oxide, the action of chlorine on arsenic, the oxidation of ether vapour and so on, have no effect on the electric conductivity of the gases. I found, too, that even when the combination was as vigorous as that between hydrogen and chlorine in the light, no effect whatever was produced on the electrical conductivity of the mixture. Again dissociation at moderate temperatures such as that of nickel carbonyl at about 100° C. into nickel and carbon monoxide, or in the dissociation of arseniuretted hydrogen, is quite without effect on the conductivity. This is in accordance with the consequences of the theory.

There are, however, some cases in which free gaseous ions are produced by dissociation or chemical action. Thus Kalendyk [19] found that the vapour of potassium iodide was a conductor of electricity at temperatures above 300° C. if damp, but not when dry; this is a good example of the effect of water vapour. Another case investigated by Bloch (*loc. cit.*) is the oxidation of P_2O_3 to P_2O_5, which is also accompanied by an increase in electrical conductivity.

The efficacy of polar molecules is on this view due to their large electrostatic moment, which causes them to be strongly attracted by other molecules. Any systems, such as free electrons or gaseous ions, which give rise to strong electric fields, might be expected to promote chemical combination by processes similar to those which occur with water molecules.

Again, if the reacting gases were condensed on the surface of a piece of metal, or on the surface even of a non-metal or liquid, particularly if these substances were of special types, the molecules would find themselves in the presence of agents of the kind we are considering. At the surface of a metal there are mobile electrons, while the molecules at any surface can only be coördinately saturated in very exceptional cases. For when a new surface is produced by fracture some of the atoms which helped to "satisfy" the molecules left behind have been torn away, so

[18] *Annales de Chimie et de Physique*, **22**, pp. 370, 441; **23**, p. 28.
[19] *Proc. Roy. Soc.*, **A90**, p. 638, 1914.

that the molecules on the surface must be unsaturated and able to bind other atoms or molecules. The energy derived by the approach of a molecule to the unsatisfied molecules at the surface of the solid or liquid may be used to separate the atoms in the approaching molecule, in just the same way as the energy due to the approach of a polar molecule helped to separate them. Thus the molecules of a gas condensed in a layer on a surface will be exposed to influences very similar in character to those to which they would be exposed when combined with water molecules, and we may expect to find that the connection between these atoms gets so loose that these are able to rearrange themselves and form new compounds.

The layers condensed on a surface will in many respects be in a more favourable condition for entering into chemical combination than the free molecules of the gas, even if these are supplied plentifully with water molecules. For the molecules in the surface layer will be crowded together and kept in close contact; they will thus be in a situation particularly favourable for the rearrangement of their atoms.

The effect of metal surfaces in promoting chemical combination is shown by the combination of hydrogen and oxygen produced by platinum black, by the synthesis of ammonia in the Haber process, by the effect produced by metals when in the colloidal state, by the Sabatier-Senderens method, where many changes in organic compounds are produced by passing them along with hydrogen over finely divided nickel or certain other metals at a high temperature. Another instance is the effect produced by the walls of the vessel in which the reacting gases are contained; many examples of this are given by Van t'Hoff in his studies on chemical dynamics.

It is possible that water in addition to the effect it produces by its individual molecules may produce an additional effect by forming small drops, which in the aggregate might have a very large surface, on which the gases might condense.

We can get some very direct evidence as to the conditions at the surface of separation of gases, liquids and solids by the study of the very interesting cases of electrifications produced by the bubbling of gases through liquids, by the splashing of liquids against solid surfaces, and the motion under an electric

field of bubbles of air, and colloidal particles through liquids. When gases bubble through certain liquids of which water is a conspicuous example, the gases after they emerge from the liquid are found to be electrified. The liquids which give rise to this electrification are those which possess considerable electrical moments, *i.e.*, they are those which, as we have seen, have the property of forming complex compounds with compounds which are already electrically saturated. The amount, and even the sign of the electrification produced by bubbling, is very sensitive to small changes in the composition of the liquid. Thus air bubbling through pure water emerges with a negative charge, but if a small quantity of HCl or H_2SO_4 be added to the water, the electrification of the air becomes positive. The electrification is dependent upon the breaking of the liquid film when the air bubble escapes from the fluid. No electrification is produced by blowing a current of air along a water surface or by stretching, without breaking, a liquid film. A similar dependence upon the composition of the liquid is shown by the motion through a fluid of small particles or air bubbles under an electric field, a phenomenon which is sometimes called cataphoresis. The addition of acids and salts, especially if these contain elements of high valency, produces a great effect on the velocity with which the bubble moves through a liquid under a constant electric field. Cataphoresis is more amenable to mathematical treatment than electrification by bubbling and the mathematical theory has been worked out by v. Helmholtz and Lamb on the supposition that there is a double layer of electricity, one layer being positive and the other negative, at the surface between the bubble and the liquid, and that one layer is attached to the liquid, the other to the bubble or colloidal particle. If v is the velocity of a particle under an electric force X, η the coefficient of viscosity of the liquid, σ the surface density of the electric charge on either layer, d the distance between the layers, then according to v. Helmholtz

$$v = \sigma d X/\eta \qquad (29)$$

so that the measurement of the velocity would at once give us the potential difference at the surface. Lamb has given very strong reasons for thinking that this relation is not sufficiently general and is based upon suppositions which are not likely to be valid when, as in this case, we are dealing with distances which are of

the order of atomic distances; he finds instead of (29) the equation

$$v = \sigma l X/\eta \qquad (30$$

where l is a length dependent on the liquid and on the nature of the particle. As l is not known, we cannot claim that the use of the v. Helmholtz formula gives more than the order of the surface density, in some cases, however, where it has been possible to measure the potential difference between the particle and water, this has been in fair agreement with the value deduced by Helmholtz's equation. It will be noticed that according to either formula the velocity of the particle is independent of its size, provided σd and σl are unaltered. This has been verified by several observers, among others by Burton[20] and McTaggart.[21] In water, air bubbles and some solid particles move as if the negative charge were on the particle, and it is remarkable that, in spite of great variations in the character of the particle, the changes in the potential difference are comparatively small. This is shown in the following table taken from Burton.[22] The potential difference φ has been calculated from the v. Helmholtz equation assuming

$$\varphi = 4\pi\sigma d/K$$

where K is the specific inductive capacity of water.

Substance.	Potential Difference in Volts Deduced by Helmholtz's Equation.
Lycopodium	−.035
Quartz	−.042
Air bubbles	−.056
Arsenious sulphide	−.031
Prussian blue	−.056
Gold (Bredig)	−.030
Platinum (Bredig)	−.028 − .034
Silver (Bredig)	−.033
Mercury (Bredig)	−.035
Bismuth (Bredig)	+.015

We see from this list that for many substances the difference of potential between the two layers is about 1/30 of a volt; this is very nearly the potential difference through which an electron must fall at room temperatures to acquire an amount of energy equal to that possessed by a molecule of gas from its thermal

[20] "Physical Properties of Colloids," 2nd Edition, p. 136.
[21] *Phil. Mag.*, **27**, p. 297 (1914).
[22] "Physical Properties of Colloids," p. 135.

agitation. Thus a charged atom at the double layer would possess by thermal agitation an amount of energy comparable with that required to detach it from the double layer. We should expect that a limit to the potential difference between the two layers must be imposed by the necessity of one layer being able to move freely relatively to the other. If, for example, the double layer were formed by positively and negatively charged atoms in the same molecule it could not produce cataphoresis unless some source of energy sufficient to dissociate the positive from the negative parts were forthcoming. If this energy has to come from thermal agitation, the positive and negative parts must have been driven so far apart that the energy required to separate them is of the order of the mean kinetic energy of a molecule due to thermal agitation, which at 0° C. is about 1/30 of a volt. The energy required to detach a charge from the double layer is proportional to the potential difference between the layers. Thus the energy available from thermal agitation may be a most important factor in determining the value of the potential difference in the effective double layer.

THE FORMATION OF THE DOUBLE LAYER.

Polar molecules, such as those of water, have, as we have seen, the power of forming molecular compounds in which oppositively charged atoms are separated and put into a condition in which they can be easily detached from each other. These compounds are of two types, in the first symbolized by such a case as $[Me.4H_2O.(OH)_2]H_2$, the effect of the formation of the complex compound is to give a charge of negative electricity to the substance with which the water is in contact and to put two positively charged atoms into a condition in which they can easily be detached from the substance. The formation of a compound of this type would produce a double layer with the positive part in the water and the negative on the substance. This is the type of double layer formed at the surface of colloidal particles of platinum, gold, silver, quartz or air bubbles. The other type of complex compound is that symbolized by $[Ca.4H_2O]Cl_2$, here the water molecules drive out the negative constituent from the original compound and give to the system surrounding the central atom a positive charge. If a substance of this kind were formed there would again be a double layer, but in this case the negative

part of it would be in the water, the positive on the substance in contact with the water. This is the type of double layer formed at the surface of colloidal particles of ferric hydroxide.

The case of a gas bubble in water is an interesting one in which the evidence on some points is somewhat conflicting. McTaggart found that the velocity of bubbles of hydrogen was the same as that of oxygen bubbles indicating that the potential difference was independent of the nature of the gas, and that the gas did not take part in any chemical reaction. Alty, who has recently been making experiments on this point in the Cavendish Laboratory, finds that considerable variation in the velocity of the bubbles is produced in some cases by changing the gas. The view that oxygen may take part in chemical reactions with water is supported by the observation frequently recorded but first made, I think, by Bellucci,[23] that the air in the neighbourhood of waterfalls, where there is a great deal of splashing, contains abnormally large quantities of ozone. Under the action of the water molecules ozone may be formed and negatively electrified ozone form the coating in the gas of the double layer.

We should expect that there would be a double layer at a surface separating water from its own vapour. Hardy and Langmuir have pointed out that the molecules at a liquid water surface are polarized, *i.e.*, the number of molecules which have their positive ends at the top is not the same as the number with the negative end. Thus, suppose the majority of molecules had the negative ends, *i.e.*, the oxygen atom, at the top, the oxygen atoms are not coördinately saturated and may combine with the molecules of water vapour to form compounds of the type $[O.H_2](OH)_2$: This would give rise to a double layer with the positive half in the water, the negative one in the bubble. Experiments are in progress at the Cavendish Laboratory to see whether any evidence can be obtained of a double layer when water is in contact with nothing but water vapour.

The formation of the double layer gives a supply of positive and negative ions at the surface of an air bubble in water. Just before the bubble emerges from the water this surface has a considerable area. It is reduced to very small dimensions after the bubble emerges. Thus the emergence of the bubble involves a

[23] *Ber. Deutschen Chem. Gesell.*, **8**, p. 905 (1875).

considerable and very abrupt contraction of the surface and of the double layer associated with it. The double layer will be violently distorted and it does not seem surprising that some of the ions in the layer on one side should not have time to combine with those on the other before they are carried away by the air. Only a very small fraction of the ions in the double layer get liberated when air bubbles through water. Assuming v. Helmholtz's formula, we can calculate from the velocity of the bubble the quantity of electricity per unit area of each layer. Assuming that the distance between the layers is 10^{-8} cm., McTaggart (*loc. cit.*) found that this density was 4×10^{-5} coulombs per square centimetre. If all the water molecules had been polarized, *i.e.*, if all the OH ions of the water molecules were next the surface and if the distance between two molecules of water on the surface were the same as that in the interior, *i.e.*, 3.09×10^{-8} cm., the density would be about 1.7×10^{-4} coulombs per square centimetre, about four times greater. On one layer of a bubble 7.8 mm. in diameter the charge on either layer would be 7.6×10^{-5} coulombs. Simpson [24] found that when a drop of this size struck against a plate the amount of electricity set free was 2.8×10^{-12} coulombs, *i.e.*, only about one thirty-millionth of the charge on the layer. We conclude from this that only an exceedingly small fraction of the water molecule at the surface of an air bubble or drop of water is ionised by the bursting of the bubble or the splashing of the drop.

When air bubbles through water some ions become free, there are other types of experiments when, though there is a separation of positive and negative electrification, few if any ions get free. The Armstrong hydro-electric machine is a case in point. Here small drops of water are carried by a jet of steam through a tube with great velocity. In their passage through the tube the drops strike against the sides and the tube becomes negatively, the drops positively, electrified. Here the separation of the positive and negative electrification is the principal effect and not the liberation of free ions. We have supposed that at the surface of a drop of water there is a double layer, the negative part, OH ions, in the air and the positive part, H ions, in the water. When the drop strikes against the tube the OH ions combine with the material of the wall of the tube forming those

[24] *Phil. Trans.*, 209A, p. 379 (1909).

molecular compounds we have been considering in this chapter. When the drop rebounds from the wall of the tube it will tend to take the H_+ ions away with it, while the walls of the tube will hold the OH_- ions. The ions will be separated by the kinetic energy of the drops. The ions will not, however, get free; the positive ones will be on the water drops and the negative ones on the walls of the tube. This is a particular case of electrification by friction, and it is evident that the formation of double layers must be of vital importance in that phenomenon

ACTIVE MOLECULES.

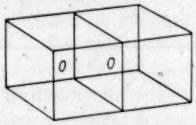
We have hitherto considered the way in which chemical combination was promoted by polar molecules and by active surfaces, the energy necessary for the preliminary separation of the atoms in the reacting molecules before their final readjustment to form the molecules of the new compound coming from the potential energy of separation of the polar molecules and of the reacting molecules before combination. We have seen that the kinetic energy of thermal agitation is inadequate for this purpose. Though the influence of polar molecules on chemical combination is undoubtedly very great, the evidence does not, I think, warrant the conclusion that all chemical combinations are dependent upon their agency. The combustion of carbon bisulphide, of cyanogen and of certain hydrocarbons in oxygen appears to be unaffected by the presence of traces of moisture.[25] The question arises, what is the mechanism by which the combination can be brought about, when the energy arising from polar molecules is not available, and when that due to thermal agitation is too small to split up the molecules of the reacting gases into atoms? The electron theory indicates a way in which certain molecules could be put into a chemically active state without separation into atoms by an expenditure of energy much less than would be required for that purpose. Consider, for example, a molecule of oxygen, its neutrality is attained by the arrangement of its electrons into two octets, to obtain these two the utmost economy in construction must be observed and the octets have to have four electrons in common. Let the electrons in the molecule be displaced so that the cells surrounding the atoms have no longer four electrons in common, suppose, for example, that they have only two in com-

[25] H. B. Baker, *Proc. Manchester Phil. Soc.*, 53, No. 16.

mon, then since there are only twelve electrons available there can only be seven electrons in each cell, and each atom will be surrounded by only seven electrons instead of by eight. Now the cell of seven electrons is not saturated and will be chemically active, though it will not be so unsaturated as the free oxygen atom which is only surrounded by six electrons. To move the electrons so as to change the arrangement of electrons from that corresponding to the inactive state represented by Fig. 34 to that of the active state represented by Fig. 35 would require far less energy than to separate the atoms, so that the necessary amount may be derivable from thermal agitation at temperatures far below that required to separate the atoms.

I think this conception of the active molecule has an important bearing on the combination of explosive mixtures such as those of

FIG. 34.



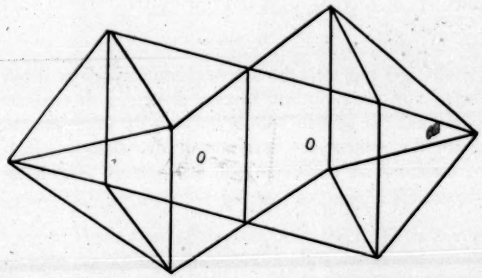
oxygen and hydrogen; these gases explode at temperatures as low as 600° C. where the energy of thermal agitation is quite insufficient to split the oxygen molecules up into atoms. Indeed, direct experiments on the relation between temperature and pressure have shown that there is no appreciable dissociation of the molecules of oxygen at 1700° C. If, however, the work required to make the molecule active in the manner described was that corresponding to thermal agitation at a lower temperature, say 600° C., then if in any region of a mixture of the explosive gases the temperature reaches this value, the oxygen molecules will become active and combine with the hydrogen, the heat developed by the combination will raise the temperature still further and the hot molecules will travel out with energy sufficient to make the molecules of oxygen against which they strike active. This will lead to further combination and a further development of heat and combination will spread throughout the mixture.

As there is no dissociation of the molecules into atoms, the process of making the oxygen molecules active will not change the pressure in pure oxygen.

There is direct experimental proof that the molecule of oxygen can be put into the active state. When we use the method of positive rays we find that oxygen is one of the few molecules, as distinct from atoms, that can occur with a negative charge. If the oxygen molecule could only occur with its electrons arranged as Fig. 34, it could not receive a negative charge, because there is no room for an electron in the octets. It could, however, receive such a charge if the electrons were arranged as in Fig. 35 because there is room for an electron on each of the septets.

The fact that a particular atom or molecule can be negatively charged, shows that it can be in stable equilibrium after receiving

FIG. 35.



an additional electron, so that in the neutral state it is unsaturated and chemically active.

The arguments we have used about the oxygen molecule will apply to any arrangement of electrons where there are two octets with four electrons in common. This arrangement occurs when we have two atoms connected by a double bond—it occurs, for example, in carbon compounds whenever there is a double bond between two carbon atoms, C = C, it also occurs in the combination C = O, though not in C — O – H.

THIELES' THEORY OF PARTIAL VALENCIES.

This conception of the active molecule leads in many cases to the same results as Thieles' theory of partial valencies. Thus to take the case which led to the theory. It was found that a compound where the carbon atoms are arranged according to the

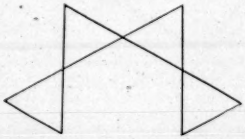
scheme C – C – C – C, where two double bonds are separated by a single one, when it forms additions compound does so by adding the new atoms to the carbons at the *ends* of the chain. On our view the distribution of the electrons in the compound is represented in Fig. 36.

There are four octets, 1, 2, 3, 4; 1 and 2 and also 3 and 4 have four electrons in common, 2 and 3 only two. Suppose all the

FIG. 36.

carbon atoms get put into the active condition. The octets with four electrons in common will become septets with two electrons in common and the system will be a chain of four septets (Fig. 37), where the septets are represented by triangles, each having two electrons in common with its nearest neighbour. To

FIG. 37.



make this change in which all the carbon atoms have been made active requires the expenditure of a certain amount of energy; an expenditure of a smaller amount will be sufficient to make a part of them active. To find the change which will require the least energy, we notice that if any adjacent pair of septets were to revert to a system with four electrons in common, the new system would have less potential energy than that shown in Fig. 37, and would require less energy to be expended to derive it from the original system.

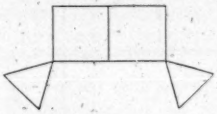
The work required for this change would be the work required to convert the system (Fig. 36) into the system (Fig. 37), minus the loss of potential energy when an adjacent pair of septets

reverts to two octets with four electrons in common. Thus the system which will require the minimum work will be the one when the pair which reverts is the one for which the loss of potential energy on reversion to octets is greatest. This pair will be the one which is most symmetrically placed, *i.e.*, the central pair. Thus the active configuration which requires the least expenditure of work is that represented in Fig. 38, where the end cells are septets and active. As these cells are active, additions will take place at them, and the central carbons will be connected by a double bond.

KETO-ENOL CHANGE.

The same reasoning will apply where the double bond is between a carbon and an oxygen atom. Thus in the compound

FIG. 38.



$O-C-C-H$, the distribution of electrons is that represented in the figure, if the two octets with four electrons in common are made active, the active oxygen units with the neighbouring atom of H, the hydrogen coming away from C_2 with its electron; this completes the octet round O, leaving septets round C_1 and C_2 with two electrons in common; these revert to the more stable arrangement of the same number of electrons, *viz.*, two octets with four electrons in common, and we have thus the compound

$$OH-C=C$$

this is known as the keto-enol change. It only takes place when one of the atoms attached to C_2 is that of an electronegative element; the reason for this follows from the same considerations as those previously given to explain the effect of introducing electronegative groups into hydrocarbons.

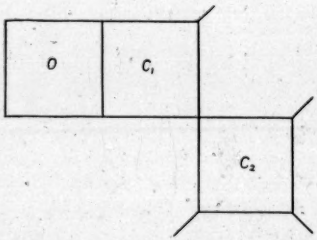
The same principles will apply to a smaller extent when two octets have only two electrons in common, for if the electrons were displaced so that the cells had only one electron in common, one of the atoms would become active and could enter into chemi-

cal combination. Thus, if the electrons in a chlorine molecule get displaced so that the cells have only one electron in common instead of two, one of the cells will become active and can combine with hydrogen. The energy required to displace the electrons need not come from the energy of thermal agitation, it might come from light if that were absorbed by the molecules.

PRODUCTION OF LIGHT BY CHEMICAL CHANGE.

Many chemical reactions involve an increase or a decrease in the number of electrons grouped round some of the atoms; thus, for example, if an atom of hydrogen combines with one of

FIG. 39.



chlorine to form HCl, after combination the chlorine atom is surrounded by eight electrons, whereas before it was surrounded by only seven, thus the reaction has resulted in an electron falling into the layer round the chlorine atom; this atom may be regarded as coming from the hydrogen atom. On the other hand, when HCl dissociates into H and Cl the chlorine ion loses an electron, while the hydrogen ion gains one. We shall use the term oxidation for the process by which the atom of an electronegative element gains an electron and becomes negatively charged since ordinary oxidation is a process of this kind, and reduction for the process by which a positively electrified ion of an electropositive element receives an electron and becomes neutral.

Thus, in oxidations an electron falls into the zone round the atom of an electronegative element; in reductions an electron falls into the zone round the atom of an electropositive one. From the study of the luminous effects in the discharge of electricity through gases we are led to the conclusion that the capture of

an electron by an atom results in the emission of light, and from the quantum theory it would follow that the frequency of the light would be proportional to the potential energy lost when the electron falls into the atom, or what is equivalent, to the work required to remove an electron from the negatively electrified constituent of the compound in the case of oxidation or from the neutral atom in that of reduction. Thus we should expect that both oxidation and reduction would be accompanied by the emission of light; it may be that the rate at which the chemical processes go on is so slow that the energy in the light is not sufficient to make it apparent, or again, that the wave-length of the light is not within the range of the visible spectrum. The production of light by chemical action is a well-known phenomenon. In addition to the conspicuous cases of flames where the temperature is high, there are many examples of luminosity occurring at moderate temperatures; the luminosity of phosphorus when oxygen passes over it is one example; then there is the luminosity of sulphur when heated to about 300° C. in the presence of oxygen, the light given out by the glowworm and by the animalculæ which cause the phosphorescence of the sea. Linneman found that fresh surfaces of sodium or potassium are luminous in the dark until they get covered by a coat of oxide. This production of light is, I think, the cause of the emission of electrons in the dark from the alloy of sodium and potassium when exposed to various gases which I observed many years ago and which has been investigated very fully by Haber. If chemical action went on between the gases and the NaK alloy, light would be given out, and as the alloy is very photoelectric, electrons would be given out by the surface of the alloy. The seat of the light is at the surface of the alloy so that, although the light might not be intense enough to be visible at molar distances, yet at the atomic distances which separate it from the alloy its intensity might be sufficient to produce very considerable effects. Again, since in oxidations the origin of the light is in the electronegative elements, we should not expect to find in light due to oxidation the spectrum of the electropositive element. It has long been considered remarkable that the spectrum of hydrogen is not visible in flames or in light produced by chemical means, though it is so easily produced by the electric discharge. This is just what we should expect if the chemical reactions were of the type of oxidations; to have

a chance of getting the hydrogen spectrum the process should be a reduction. Thus, for example, in the partial dissociation of hydrodic acid, when there is equilibrium between the formation of HI and its dissociation into H and I, the combination would give rise to the spectrum of HI with the iodine as the source of light, the dissociation might give the hydrogen spectrum. It is to be noted that the spectrum of a molecule may vary with the atom in that molecule which is excited. Thus to take as an example $COCl_2$, the spectrum emitted due to the fall of an electron into the oxygen atom would not be the same as that due to the fall of one into the chlorine atom. We have in considering the type of light emitted to consider not merely the atom into which the electron falls, but also the method in which it falls. Thus to take a case in which we have very vigorous reduction going on, that of the liberation of hydrogen from the cathode when strong currents pass through acidulated water. Since the hydrogen atoms which come off are neutral, the hydrogen ions which were positively electrified must each have received an electron and so might be expected to have given out light. I am not aware, however, that anyone has observed any luminosity in the neighbourhood of the cathode during the electrolysis of acidulated water. Nor need we, I think, expect it; we have already seen reasons for thinking that hydrogen ions in water have attached to them a number of water molecules, the negative ends of these molecules being turned towards the hydrogen ion. The effect of these negative charges is to diminish very materially the attraction of the hydrogen ion on the negative electron, so that when the electron falls into the ion it will do so with very much less energy than it would in the absence of the water molecules; as the energy is so much less, the intensity of the light and also its frequency will be greatly diminished, so that not only will the light be feeble, but also probably far away, on the red side of the visible spectrum.

ON HOMOLOGOUS ELEMENTS AND VARIABLE VALENCY.

Homologous Elements.—The valency of an element depends according to these views on the number of electrons in the outer layer rather than upon the total number of electrons in the atom. We have supposed that the electrons in the atom are arranged in a finite number of layers, the members of each layer being approximately at the same distance from the centre of the atom.

As we pass from the atom of one element to that of the element next in order of atomic weight, we have to provide for the accommodation of one more electron in the atom. If the additional electron joins those in the outer layer it will give rise to an atom of an element of different valency and with very pronounced difference in chemical properties. If, however, the electron finds accommodation in one of the layers below the surface, the element corresponding to this atom will have the same valency as the first and will resemble it in chemical properties more or less closely according as the layer on which the new electron settles is near to or far from the centre of the atom. Thus we might have a graduated series of elements differing in atomic weight; the properties of some—those with the additional electrons in the layers close to the centre differing so little from those of some element of smaller atomic weight in the series that the two might with propriety be regarded as isotopes. The difference in properties will increase though the valency remains unaltered, as the electrons find a place in layers nearer the surface until finally we come to the element where the additional electron has got to the outer layer; here there is a change in the valency and a marked alteration in the chemical properties. We are thus led to expect the existence of groups of elements possessing very similar properties; in some cases the chemical properties might be so similar that the elements would not be separable by chemical means and would be classed as isotopes; in others the differences would be large enough to enable the elements to be isolated by chemical processes. Examples of such groups are the iron, nickel and cobalt group, the ruthenium, rhodium and palladium group, the large group of the rare earths and the iridium platinum group. Inside these groups, increase in atomic weight is not accompanied by change of valency; outside them, it is.

In considering the way in which a definite number of electrons will arrange themselves round a central charge, there are two influences of predominating importance: The first of these is the tendency of the electrons to get as close to the central charge as is consistent with the stability of the layer, *i.e.*, to have as many electrons in the innermost layer as the central charge can hold in stable equilibrium, and then as many in the second layer as the central charge when surrounded by the first layer can hold in stable equilibrium, and so on. This disposition will make the

potential energy due to the forces between the positive nucleus and the electrons as small as possible. The potential energy due to the forces between the electrons has next to be considered. This will diminish as the distances between the electrons increase and will tend to make the electrons in the various layers arrange themselves so that their figures are similar, or at any rate have the same kind of symmetry about the centre. This latter tendency would, if it prevailed, cause a new electron if added to an atom already containing a number of electrons either to go to the outer layer, or if that were full, to make the beginning of a new outer layer. The tendency to get as close as possible to the centre would, on the whole, make for the retention of the electron by one of the inner layers.

We should expect that we could not go on increasing the number of electrons without reaching a stage where a new electron would stay in the inner layers. If so, its influence on the chemical properties would be very slight and the new element would be very similar to the old. The addition of an electron to one of the inner layers would alter the nature of its symmetry round the centre and make it different from that of the other layers; as the different layers like to have the same kind of symmetry, when one layer has got a new electron the others will try to get one, too, so that when once the absorption of electrons by the inner layers has begun it will continue as the next few electrons are added to the atom. When each layer has received an electron, we may expect the next electron to come to the surface, giving rise to an element whose properties are markedly different from those of the elements which just preceded it. Thus the homologous elements might be expected to occur in groups and inasmuch as in the elements inside the group, some of the layers have one kind of symmetry and others a different one, the distribution of electrons inside the atom of elements in a homologous group is irregular and does not possess the uniformity or regularity possessed by elements outside the group where the electrons in the inner layers have adjusted themselves so as to produce a high degree of symmetry.

Varying Valency.—We have been considering cases where different elements have very similar chemical properties, although they contain different numbers of electrons, where, in fact, we have variations in the number of electrons in the atom without

much alteration in the chemical properties. The question naturally arises whether we might not have also variation in the chemical properties without alteration in the number of electrons, and whether the existence of some elements which have more than one kind of valency is not a case in point. Ferrous and ferric iron have different properties, so have cuprous and cupric copper. As the elements can pass backwards and forwards between the -ous and the -ic states, if these states correspond to two different configurations of the same number of electrons, these configurations must be such that by suitable chemical or physical processes they can pass from one form to the other. We have already seen that there are frequently more ways than one of arranging in stable equilibrium a given number of electrons round a central positive core. If these arrangements are to explain the difference between the -ous and -ic states of the elements, they must differ in the arrangement of the outer layer (*a*) because unless they did so there would not be sufficient difference in the chemical properties in the two states, and (*b*) because if the difference was only in the inner layers we could not affect these sufficiently by ordinary chemical operations to cause one configuration to pass into the other.

We should expect, I think, to find forms of the same kind of atom differing in their outer layers in those elements which are either in a group of homologous elements or in their immediate neighbourhood. For in the atoms of such elements an electron hesitates, as it were, whether to go to the surface or to stay in one of the inner layers, *i.e.*, it hesitates between two different configurations. It is reasonable to suppose that by suitable influences at the surface the electron might be induced to take one course or the other and thus confer one valency or another on the atom of which it is an occupant. Now it is remarkable that many of the elements which are most conspicuous for the variability of their valency are either in the homologous groups or in their immediate neighbourhood. Take, for example, chromium and manganese, which are the next neighbours of the iron groups, each of these shows great variations in valency in its different compounds, then molybdenum, the next neighbour to the ruthenium, rhodium and palladium group forms the series of chlorides $MoCl_2$, $MoCl_3$, $MoCl_4$, and $MoCl_5$; again tungsten, the next neighbour to the platinum and iridium group, forms the four

chlorides WCl_2, WCl_4, WCl_5 and WCl_6, and nearly, if not quite, all of the elements in the homologous groups themselves form more than one series of salts. The electrons in the outer layers of elements of this type seem to be in a peculiarly sensitive condition and can move from one layer to another without much expenditure of energy.

The number of electrons which can be held in stable equilibrium in a single layer by a positive charge increases with the charge. Thus, though an inner layer of eight might be as many as the positive charge possessed by the lighter elements could stabilize, yet the heavier elements with their large positive charges might be able to stabilize more than this number. We should thus expect that at some stage in the list of elements the number of electrons in the inner layers would increase, that while when we pass from one element to the next and the number of electrons in the atom increases the additional electron stays in the inner layer instead of going to the one on the outside of the atom. When this process begins the change from atom to atom will not be the addition of an electron to the outer layer, but a reorganization of the distribution of electrons in the interior of the atom. The properties of the elements indicate that this process begins soon after passing calcium. To illustrate the point, I will take the series of elements beginning with titanium and consider the arrangement of electrons in it and the neighbouring elements. I do not lay any stress on the actual numbers of electrons assigned to the inner layers; the determination of these would require much further investigation, both theoretical and experimental.

Titanium.—The distribution of electrons, if it followed the same course as in the lighter elements, would be represented by 2, 8, 8, 4, the figures representing the number of electrons in the different layers starting from the inside; the four electrons in the outer layer would make the element quadrivalent. The existence of the tetrachloride $TiCl_4$ shows that this distribution is one which occurs in nature. In addition to the tetrachloride there are the chlorides $TiCl_3$, $TiCl_2$, showing that forms of the titanium atom exist in which there are respectively one and two more electrons in the inside than in quadrivalent titanium, the distribution of electrons in the tautomeric forms may be represented by 2, 9, 8, 3, and 2, 10, 8, 2, respectively.

Vanadium.—If the electrons had followed the normal course,

the arrangement of the electrons would be represented by 2, 8, 8, 5, and the element would be pentavalent. Vanadium is said to form a pentafluoride VF_5, so that this configuration would seem to exist. Vanadium forms chlorides VCl_4, VCl_3, VCl_2, in which the inner layers of the atom must contain respectively one, two and three electrons more than the preceding case; thus we have atoms in which the arrangements are 2, 9, 8, 4; 2, 10, 8, 3; 2, 10, 9, 2, respectively.

Chromium.—If the electrons followed the normal course the arrangement would be 2, 8, 8, 6, and the element would be sexavalent; the compound CrF_6 shows that this type exists. Chromium forms the chlorides $CrCl_3$, $CrCl_2$, so that in addition there are atoms of the type 2, 11, 8, 3; 2, 12, 8, 2, respectively.

Manganese.—The normal arrangement would be 2, 8, 8, 7. The fluoride MnF_7 shows that this type exists. There are in addition the fluorides MnF_4, MnF_3, MnF_2, corresponding to atoms of the type 2, 11, 8, 4; 2, 12, 8, 3; 2, 12, 9, 2.

Iron, Nickel and Cobalt.—From the similarity of these elements we infer that the distribution of electrons only differs in the inner layer. Their halogen compounds are all of the type $FeCl_2$ or $FeCl_3$; suggesting the following distribution of electrons:

Fe	2, 12, 10, 2, 2, 12, 9, 3
Ni	2, 13, 10, 2, 2, 13, 9, 3
Co	2, 14, 10, 2, 2, 14, 9, 3

Copper.—The halogen compounds are of the type CuCl, $CuCl_2$, indicating atoms with one or two electrons, respectively, in the outer layer, corresponding to distribution of electrons represented by 2, 14, 12, 1; 2, 14, 11, 2.

The normal process by which, when we pass from one element to the next in order of atomic weight, the new electron goes to the outer layer seems to be resumed after passing copper, thus we have zinc with two electrons in the outer layers; gallium with three; germanium with four; arsenic with five; selenium with six; bromine with seven, and krypton with eight.

Thus we see that as we proceed up the list of elements we may expect to meet with a batch of elements in whose atoms the electrons change from one tautomeric distribution to another with but little expenditure of energy. In this batch the ordinary progress of valency with atomic weight is interrupted, and the

valencies are variable. On passing through the batch the regular sequence is resumed, the series goes on and ends with eight electrons on the outer layer, while the next series begins with one in that layer.

Paramagnetism.—One very conspicuous feature of the elements from titanium to copper is that they are strongly paramagnetic. The quality of paramagnetism would on several theories depend on a want of symmetry in the arrangement of the electrons in the atom. This would be the case, for example, in Parson's theory of the ring electron; it would also follow from the law connecting electrostatic and magnetic force which I suggested some time ago.[26]

If want of symmetry in the distribution of electrons is essential for paramagnetism, we can understand why it is confined to elements such as those we are considering, where the arrangement of the electrons in the inside of the atom may change, not merely from element to element, but even in a particular element under different external conditions. Outside such a group of elements the arrangement of the inner electrons does not change from element to element, it is very stable, and thus has probably a high degree of symmetry. It would, from this point of view, be interesting to test the magnetic qualities of compounds like CrF_6 and MnF_7, in which the readjustment of the inner electrons has not taken place.

The researches of G. Wiedemann, Quincke, Townsend, Pascal, Weiss, Kamerlingh Onnes and others on the relation between magnetic properties and chemical composition have brought to light a great number of very striking phenomena, which are very diverse and in some cases anomalous, their very diversity, however, renders them all the more suggestive.

For salts in solution, and the same seems to be true for salts in the dry state, especially if these contain water of crystallization, the value of k, the coefficient of magnetization, *i.e.*, the quotient of the induced magnetization by the magnetic force, depends upon whether the metal is in the *-ous* or *-ic* state, but does not depend upon the acid radicle with which it is combined. Thus if a solution contains a definite amount of ferric iron the value of k will be determinate, it does not matter whether the dissolved salt is ferric chloride, ferric sulphate or ferric nitrate. The same is

[26] *Phil. Mag.*, 37, p. 419.

true for the ferrous salts; again the value of k depends only on the quantity of ferrous iron, but the value of k for the same weight of iron will depend upon whether the iron is in the ferrous or ferric state. Thus if W is the weight of iron in a cubic centimetre—

$$10^7 k = 2660W - 7.7 \text{ for ferric salts.}$$
$$10^7 k = 2060W - 7.7 \text{ for ferrous salts.}$$

In such salts as ferrocyanide of potassium where the iron appears on the negatively electrified part of the molecule, thus $\overset{+}{K}_4(\overset{-}{FeCN_6})$, the compound is not paramagnetic at all, but slightly diamagnetic. The ferricyanide $K_3(FeCN_6)$ is slightly paramagnetic, although the paramagnetism is very small in comparison with that of the ferrous or ferric salts. Similar results are shown by the magnetic metals Cr, Mn, Ni, Co. Copper itself is diamagnetic as are also the cuprous salts; the cupric salts, however, are magnetic. The oxides and sulphides of the magnetic elements show large variations in their magnetic properties, thus magnetite Fe_3O_4, which is regarded as a compound of FeO and Fe_2O_3, is much more magnetic than either of them, and a similar statement is true for the corresponding sulphur compounds. Again variation in the temperature may produce great changes in the magnetic properties of an element, thus four types of iron, α, β, γ, δ, have been detected by Osmond and other workers; these pass from one into the other when the temperature passes through definite stages, and each of these types of iron has characteristic magnetic properties. In discussing the meaning of these results we must remember that on the view that paramagnetic properties are due to the setting of magnets, or their equivalents, under the action of a magnetic force; the magnetization, unless the field is intense enough to produce saturation (a state of things which is not attained with solutions), will depend upon two quite distinct things: (*a*) The resultant of the moments of the magnets; (*b*) the restoring force which tends to keep the magnets in the position of equilibrium. A substance may have a small coefficient of magnetization either because it contains few magnets or because the restoring force is very great, so that a given external field produces but a small displacement of the magnets. Thus the difference between the coefficients of magnetization of ferrous and ferric iron may be due either to the difference of the magnetic

moments of the magnets in the atom in the two states or to a difference in the restoring force. If it is due to a difference in the magnetic moments the intensity of magnetization when the ferrous iron is saturated will not be the same as when the ferric iron is saturated, whereas if it is due entirely to the difference in the restoring force the saturation magnetization will be the same in the two cases. We can distinguish between these effects by Weiss' Theory of Magnetons as the number of magnetons is proportional to the magnetic moment. The result of the application of this theory is that the number of magnetons per atom of iron in ferrous sulphate is 27, in ferric it is 29. As the coefficient of magnetization differs more widely than these numbers, it follows that the restoring forces must be different in the ferrous and ferric salts. In the iron in potassium ferricyanide Weiss finds that there are only ten magnetons. The difference between the number of magnetons in the trivalent and divalent condition is more pronounced in chromium and cobalt than it is for iron, thus for trivalent chromium the number of magnetons is 19, for divalent 25, in trivalent cobalt the number is 17, in divalent between 24 and 26; thus in both these metals the number of magnetons in the trivalent condition is greater than in the divalent, whereas in iron the trivalent form is slightly richer in magnetons than the divalent. A very striking case of the variation of the number of magnetons with chemical composition is that of the oxides and sulphides of vanadium. Wedekind and Horst [27] give the following values for k the coefficient of magnetization and n the number of magnetons in various compounds of vanadium.

	$k \times 10^4$	n
VO	50.06	13.9
V_2O_3	13.88	10.92
VO_2	3.73	4.19
V_2O_4	0.86	2.99
VS	7.22	5.86
V_2S_3	8.95	10.00
V_2S_5	12.55	11.90
VOCl	27.16	13.18
VN	4.13	3.92

[27] *Chem. Berick.*, **45**, 263 (1911).

Thus the effect of oxygen is of the opposite character to that of sulphur, an increase in the oxygen content decreases, while an increase in sulphur content increases the number of magnetons.

Let us now proceed to see how the magnetic properties of the salts of the magnetic metals are consistent with the following assumptions:

1. That the paramagnetism of these substances arises from the atoms of the paramagnetic element, Fe. Cr. Mn. . . .

2. That the magnetic properties of these atoms arise from a want of symmetry in the distribution of the electrons in the inner layers.

3. That the distribution of these electrons and therefore the symmetry of their arrangement can be affected by intense electric forces arising from atoms with their electrons in the neighbourhood of the atom of the magnetic element, and that such forces may also affect the restoring force of the electrons in the atom, *i.e.*, the force with which the system of electrons resists any displacement from their position of equilibrium.

We shall take in the first place the very large diminution in magnetic properties which takes place when the atom of the magnetic element is a constituent of a complex salt such as $K_4(FeCN_6)$ ferrocyanide of potassium. We may point out that this diminution may take place when the magnetic element occurs in a complex with the positive charge and not merely when as in $K_4(FeCN_6)$; the iron is a member of the negatively electrified group. Thus Feytis[28] has shown that the following cobalt salts are diamagnetic—$(Co(NH_3)6)Cl_3$, $(Co(N_43)5Cl)Cl_2$, $(Co(N_43)4Cl_2)Cl$ and $(Co(NH_3)_5H_2O)Cl_3$; though in all of these the cobalt atom occurs in the positively electrified portion of the complex molecule.

What is the condition of the atom of the metal in a complex salt? Let us take potassium ferrocyanide as an example, for similar considerations will apply to all the complex salts. In potassium ferrocyanide the iron atom has lost two electrons and is surrounded by 6CN radicles, all of which are negatively electrified. Considerations of symmetry suggest that these negatively electrified radicles are at the corners of an octahedron and the iron atom at the centre. The cyanogen radicles are, using Werner's notation, in the first zone with the atom of iron and are much

[28] *Comptes Rendus*, 152, 708 (1911).

more closely attached to it than are the atoms of potassium which are in the outer zone. Thus by the close proximity of the negatively charged cyanogens, the atom of iron is exposed to an intense and very symmetrical field of force, and this would (1) give rise to a very strong restoring force; this, if there were no change in the magnetic moments, would until saturation is approached reduce the magnetization. (2) From its symmetry this field tends to make the arrangement of the electrons inside the iron atom more symmetrical and thus reduces the magnetic moment. Both effects occur, the magnetization at ordinary temperature is reduced so much that it is not able to overcome the diamagnetism which iron, like all systems containing electrons, possesses; the number of magnetons is, according to Weiss, reduced to ten, which is only about one-third of the number in an atom of ferric ion. Let us now consider simple salts either in solution or which contain water of crystallization. Since these are electrolytes, the negative constituents of the molecule, such as Cl, SO_4, NO_3, will not be in the inner zone with the iron or other magnetic molecule, but in the outer zone. Thus these negative constituents will exert but little influence on the iron atom, and thus its state and magnetic properties will be but little affected by the change of SO_4 for Cl_2 and so on. The molecules in the zone nearest to the iron atoms are water molecules; these are probably arranged symmetrically around the iron atom and it is also probable that there are six molecules of water in the inner zone. We may picture the atom of iron as at the centre of an octahedron with the water molecules at its corners. As far as the geometrical arrangements are concerned, they are very similar to those of the ferrocyanide with water molecules in place of negatively charged cyanogen radicles. As the water molecules are as a whole uncharged, while the cyanogen ones are negatively charged, we should have expected the field of force to be much stronger with the cyanogen atoms than with the water molecules, so that in the simple salt both the restoring force and the tendency to make the distribution of electrons symmetrical would be less than in the complex salt. Thus both the magnetization and the number of magnetons would be larger for the simple salt than for the complex one. In the salt where iron is trivalent, the iron atom will have lost three electrons; while in the divalent ones, it will only have lost two. Thus there

is a difference in the number of electrons in the atoms; this might of itself be supposed to affect the magnetization. In addition to this, since the charge on the trivalent atom of iron is greater than that on the divalent, its attraction on the water molecules will be greater, these will be drawn closer into the atom and will be more favourably situated for influencing the arrangement of the electrons in the atom of iron.

In the case of the oxides the conditions are more complicated, we should expect as a general result that in these compounds the closer the connection between the iron and the atoms with which it was combined the lower would be the magnetization and that anything which tended to loosen these bonds would increase the magnetization. A loosening of these bonds would, however, increase the chemical activity of the iron by rendering it easier for it to enter into other combinations, thus we should expect to find correlation between chemical activity and magnetization, a connection which is brought to light very clearly by the experiments of Pascal. From this point of view we can understand a remarkable result obtained long ago by G. Wiedemann, *viz.*, that the magnetic qualities of Fe_2O_3 were increased by mixing with it Al_2O_3; the substances are isomorphous and may combine and form a compound in which the iron is not so firmly bound to other atoms as in Fe_2O_3.

(To be Continued.)

Soaring Flight of Gulls following a Steamer. E. H. HANKIN. (*Proc. Cambridge Phil. Soc.*, Vol. xxi, Part IV.)—When a steamer is moving dead into the wind there is an ascending current at the forward end and, strange to say, another at the stern close to the vessel, while perhaps from 10 to 50 yards farther astern there is a descending current. The existence of these two currents astern has been demonstrated by letting out a length of cotton thread. This rose from the vessel at an angle of about 60° with the horizontal, stretched out parallel to the sea farther away, and still farther off descended. The soaring gulls use the descending current astern by preference. If one gets into the adjacent ascending current it has to resort to flapping to win its way into the descending stream. Gliding may take place also in the ascending windward current, but here gain of height is less rapid than in the corresponding current astern. "That a gull should soar in an apparently descending current is, perhaps, not more surprising than that a vulture should glide with gain of height in an apparently horizontal wind." G. F. S.

The Variation of Metallic Conductivity with Electrostatic Charge. F. WENNER, NYNA L. FORMAN, and A. L. LINDBERG. (*Phys. Rev.*, December, 1922.)—H. A. Perkins in 1921 said "A simple conception of metallic conduction based upon moving electrons seemed to justify the assumption that a negative charge should increase the conductivity of a circuit, and a positive charge should decrease it." He devised a method, performed the experiment and obtained results in confirmation of his hypothesis. The three investigators in the bureau have performed a similar crucial experiment and have obtained results discordant with those of Perkins. "If, therefore, the observations are reliable, we may conclude that when the potential of a practically straight, .08 mm.-diameter, copper wire, is charged from + 6000 volts to – 6000 volts, its resistance is changed, if at all, by not more than one part in 5 million, or not more than 2 per cent., of that reported for the original experiment."

A note adds that Professor Perkins has found the cause of his large result and will publish an account of a repetition of his experiment. G. F. S.

Philadelphia-Pittsburgh Section of the New York-Chicago Cable. J. J. PILLOID. (*Bell System Tech. J.*, July, 1922.)—This line, more than 300 miles long, was designed to operate in conjunction with the Pittsburgh-Chicago cable and to fit in with other fundamental cable projects. In view of the topography of the country to be traversed and of the conditions of service, small-gage, quadded, lead-covered aerial cable was decided upon. Poles twenty-five feet long are used. The cable is strung from a steel suspension strand which is normally under a tension of 7000 pounds. The sheath is of lead-antimony alloy, one-eighth inch thick. "The wires are first wrapped with dry paper for insulation and twisted into pairs and then two pairs are twisted into what is called a quad." Nineteen quads of No. 16 A. W. G. and 120 quads of No. 19 A. W. G. pure copper conductors are in the main sections of the cable. Loading coils are sealed in iron pots mounted on poles. "The improvement, insofar as the attenuation losses are concerned, varies with the type of circuit and loading coils, but with one of the No. 19 A. W. G. circuits in this cable loaded with coils having an inductance of 0.175 henry located at 6000-foot intervals, the losses are only one-third as great as in a similar circuit without the coils."

Telephone repeaters which receive small currents, amplify them and send them on without distortion are used by the hundred in the new line. These are filament-grid-plate vacuum tubes.

On the mountains 5-ton tractors were employed to transport the cable reels which weighed half as much as the tractor. Even these failed to overcome the difficulties of certain places and the cables had to be dragged for long distances. G. F. S.

ANIMAL LUMINESCENCE.*

BY

E. NEWTON HARVEY, Ph.D.

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MR. CHAIRMAN, Members of the Institute, Ladies and Gentlemen: I think everyone in this audience understands what we mean by luminescence, a light which is produced at a relatively low temperature—"cold light." The word is contrasted with incandescence, a light which always accompanies a high temperature—"hot light." In fact, we never have high temperature of liquid or solid bodies [1] without a production of light, no matter what the substance is, whereas at low temperatures, it is only under certain special conditions that light is produced. I doubt if many, however, realize how common luminescence is. I will review briefly the various types of luminescence.

If I should place my hand under a strong light, an electric lamp, the skin, and especially the finger-nails, would give off a light of their own. This light to which I refer is not a reflected light, but a light which is actually produced in the skin and nails. We cannot see it, however, under these conditions because the light reflected from the incandescent filament is so strong that its intensity overpowers the intrinsic light which would be produced. We can arrange matters, however, so that this intense reflected light is cut off from our view and only the luminescence emitted from our skin and nails is seen. We speak of this emitted light as fluorescence. The teeth, the hair, the eyes, in fact every tissue in the body will fluoresce under certain conditions, so that this phenomenon of fluorescence is a very wide-spread one, provided we use the proper means to bring it out.

Stokes devised a means of doing this. He placed the substance to be examined in a dark box with two windows at right angles to each other. One window was covered with blue glass which allows only blue light to pass through and the other was covered with yellow glass which allows no blue light to pass.

* Presented at the Stated Meeting of the Institute held Wednesday November 15, 1922.

[1] Perfectly transparent bodies give off no light at high temperatures.

If we look at a white light through the blue and yellow glass together we see nothing. All the rays are absorbed by such a combination. If we allow the white light, however, to pass into our dark box through the blue-screened window and strike the material to be examined, at the same time observing this material through the yellow-screened window, we observe that the material, for example our finger-nails, will appear luminous. This can only mean that some of the blue rays have been converted by the finger-nails into other wave-lengths, among them yellow wave-lengths, which can then pass the yellow observing screen. This experiment shows that fluorescence is a conversion of one kind of radiation into another kind which is actually emitted (not reflected) by the body in question. No luminosity would be observed in the box unless the substance were fluorescent with yellow light that could pass the screen.

Usually short wave-lengths are converted into longer fluorescent wave-lengths. The ultra-violet is converted into visible by a great many fluorescent substances. It is sometimes of interest to consider what would happen if we were transported to a totally different environment from our own. Suppose that we were placed, with the eyes we now possess, on a planet illuminated by ultra-violet light alone. One might think that total darkness would be our fate. On the contrary we should be able to see each other and practically all living things (both plants and animals) as well as many objects in the mineral world, because of this fluorescent light.

It is possible to reproduce such conditions in the laboratory by use of a strong source of ultra-violet such as the mercury arc and Woods' ultra-violet filter, which absorbs the visible and allows ultra-violet wave-lengths of about 366$\mu\mu$ to pass. As I will show you, silk, wool, bone, tendon, cartilage, horn, coral, chitin, cellulose and a host of organic substances become fluorescent in the mercury ultra-violet. We do not see the ultra-violet light from the mercury lamp but we do see visible light from the fluorescent body.

If I turn off the current, the fluorescence will cease and it appears to stop instantly. In reality we find that the fluorescent light often[2] persists for a fraction of a second, perhaps only 0.001

[2] But not always. No one has been able to measure the persistance of fluorescence of solutions.

second, after the exciting light is stopped. Instruments, phosphoroscopes, have been devised for examining this persistance of very brief duration, but we have not the time to consider these here.

If the fluorescent light does persist we call it phosphorescence and many impure sulphides (Ca, Ba, Sr, Zn) will give off light for hours after they have been exposed to previous radiation. Fluorescence and phosphorescence are essentially the same phenomenon, differentiated as they are by persistance of luminescence, whose observation we may make as short as our measuring instruments will allow.

I should, perhaps, emphasize strongly at this point that animal light production is not a fluorescence or phosphorescence in any sense, despite the fact that we often describe it as a "phosphorescence," a use of the word in quite another sense from its strict physical implication.

There are other kinds of luminescence, but many of them are too faint to demonstrate to a large audience. If we take two lumps of sugar and rub them together, or if we take sugar crystals and crush them, a light will appear, but that light is so faint you will have to experiment for yourselves to see it. This kind of light we speak of as a triboluminescence, a light due to fracture or crushing of the crystallized material. It is well shown by shaking crystals of uranium nitrate in a tube. Every time the crystals hit each other there will be a little flash of light produced, similar to that observed with sugar but much brighter.

If we take a piece of adhesive or electrician's tape and strip off the tape rapidly, you will find that at the moment it leaves the reel there will appear a faint luminescence. This may be an electric discharge or it may be a form of triboluminescence. I do not know what causes this luminescence but suggest that it may be due to the rubbing together of some minute crystals on the tape.

The last time I lectured on "cold light" some one told me that if you take a Nabisco wafer with a wintergreen flavor and break it in half, there will be a flash of light at the moment the wafer is broken. I wished to try the experiment and on going to a grocery store to purchase my experimental material, the salesman informed me there was no such thing as a Nabisco wafer with a wintergreen flavor. You may draw your own conclusions but I regret that I cannot show you the experiment. However, if you have an opportunity, you might try it yourselves.

If we take a saturated solution of common salt and add it to some alcohol or hydrochloric acid, the salt will crystallize very rapidly, and accompanying this crystallization will be the appearance of light. This is known as crystalloluminescence, and a great many other substances besides NaCl show luminescence during rapid crystallization.

If we take pyrogallic acid, such as is used in photography for developing purposes, adding to it some hydrogen peroxide and then a little potato juice, the mixture will give a luminescence. This same luminescence is obtained if we substitute various kinds of animal blood for the potato juice. The blood and the potato juice contain oxidizers which transfer the oxygen of H_2O_2 to the pyrogallol which is oxidized with the accompanying emission of light. We have a luminescence produced by a very definite chemical reaction and speak of it as a chemiluminescence. The glowing of white phosphorous in the air is a similar luminescence. Oxygen is necessary for its production and as this is very generally the case we may speak of oxyluminescences. Although the flame of a candle or oil lamp requires oxygen we have here no oxyluminescence, but oxyincandescence, the heat of combustion of tallow or oil raising the temperature of carbon particles to incandescence.

Most of you have seen the phosphorescence of damp wood at night, or fox fire. That is due entirely to the presence of a fungus in the wood. Perhaps you have seen dead fish or meat in refrigerators, glowing in the dark. This is due entirely to bacteria living on the fish or meat. These bacteria can be raised artificially on the proper culture medium, and we can transfer them from one dish to another, thus keeping the colonies alive indefinitely. They give off their light continuously day and night. Bacteria and fungi are classified as plants, and, although the title of my lecture is "Animal Luminescence," in reality the plants can produce light as well, so that we might more correctly say, "Living Luminescence," or "Living Light."

Everyone has seen the phosphorescence of the sea. To the old observers this was rather a mystery, but we now know that all luminescence of the sea is due to one or another kind of small living creature, microscopic or macroscopic in size, mostly microscopic, however. I will now show you by lantern slides some of the organisms which are responsible for this light and point out the principles of living luminescence which they demonstrate.

The luminous animals of the sea may be unicellular or multicellular, simple or complex, but they all agree among themselves and differ from the plants which produce light, the bacteria and fungi, in that they must be stimulated to luminesce. You have no doubt noticed that phosphorescence of the sea is only apparent at the prow or stern of a ship where the water is violently agitated. Agitation serves as a stimulus to the minute creatures in it. Even the fire-fly gives off light on stimulation only, but in this case the stimulation is not mechanical, but nervous, arising in the nerve cells of the animal, just as voluntary contraction of our own muscles comes from nervous stimuli arising in the central nervous system.

The only exception to this rule is found among certain fish. I have said that dead fish very often become luminescent at night, which is due to luminous bacteria growing on them, but living fish may also produce light as well, and that is due to luminous organs in the fish. Certain forms which live in the East Indies, in one particular group of islands, the Banda Islands, have a large luminous organ under the eye, about one-fifth the length of the fish itself. This fish, *Photoblepharon*, is rather unique among animals in that the luminous organ produces its light continuously day and night and does not have to be stimulated to luminesce, but as the fish swim through the water they are constantly flashing, turning the light on and off so that they present a truly interesting picture. This is due to a sort of third "eyelid," a fold of black pigmented skin which can be drawn up over the luminous organ, thus shutting off the light.

When we study *Photoblepharon* carefully we find that the organ is made up of a mass of living bacteria. These bacteria will not live on ordinary culture media, and the fish is never found without them so that we have a true symbiotic relationship, and a mode of light production quite different from other forms. As the light of *Photoblepharon* is really due to luminous bacteria which belong in the plant kingdom, perhaps we need not regard it as an exception to the general rule that animal light appears only upon stimulation of the luminous tissue.

Other fish and certain kinds of shrimp and squid possess a row of luminous organs along the sides of the body which look like the port holes of a ship at night. In them a luminous substance is manufactured by the fish or shrimp or squid which gives

off the luminescence. There are no luminous bacteria in these organs. They often possess a complicated lantern-like structure for directing a beam of light. If we study their microscopic structure we find a picture something like this: A large amount of clear transparent tissue which is shaped like a lens to direct the light; a group of cells, called photogenic cells, in which the light is produced; a layer of cells below the photogenic cells which serve as a reflector; outside of and surrounding most of the organ another layer of cells containing a black pigment which form a screen and protect the tissues of the animal from its own light. Apparently even the light which the animals produce is injurious to them and they must have some way of protecting themselves. These organs were formerly supposed to be eyes, before it was known that they produced light.

I can only briefly mention other light-producing groups of animals—molluscs, beetles, flies, centipedes, crustaceans, brittle stars, earth-worms and marine worms, comb-jellies, jelly-fish, sea-pens, hydroids and the host of microscopic forms. Each group presents an interesting structural study, ably described by Dahlgren in the JOURNAL OF THE FRANKLIN INSTITUTE.

Those forms are most favorable for chemical study, which secrete a luminous material outside of the body (extracellular luminescence) as contrasted with those that produce light within the photogenic cells themselves (intracellular luminescence). One small creature, *Cypridina*, a crustacean about one-eighth of an inch long, has proven unusually good for chemical investigation and I will point out some of the discoveries which have been made on this material.

Our chemical knowledge has advanced in four important steps. The first step was made by Robert Boyle, in 1667, who showed that bioluminescence is always dependent on oxygen. He placed a small piece of phosphorescent wood in his air-pump and found that as he removed the air the luminescence disappeared, only to reappear again when air was readmitted. Of course at that time he did not know that the oxygen of the air was responsible, but I think we can credit him with the discovery that oxygen is necessary for luminescence.

The next step was the determination that almost any luminescent tissue could be dried, and, if dried rapidly, preserved unchanged for a long time. If, at any later time, moisture is added,

the light would appear. This was first tried on jelly-fish by an Italian, Spallanzani, in 1794.

The third important step was made by a Frenchman, Dubois, in 1865. Dubois found that in a mollusc, *Pholas,* there are really two substances necessary for light production, in addition to the oxygen and water already mentioned. One, which he called luciferin, is oxidized in the presence of the second, called luciferase, an enzyme. Enzymes are of the same nature, as you know, as the catalysts. These two substances can be separated from each other by marked differences in properties. The one which oxidizes with the production of light, luciferin, is not destroyed on boiling, so that if we wish to obtain a solution of luciferin we will make a hot water extract of the luminous animal. The hot water will destroy the luciferase, which has the properties of enzymes in general, among them destruction on boiling. If we wish to obtain the luciferase in solution we make a cold water extract of the luminous animal. Such an extract will contain both luciferin and luciferase and will luminesce for quite a while, but in time the light will disappear and that is, of course, because the luciferin is being continuously oxidized and is finally used up. The luciferase, being an enzyme, is not used up and remains in the cold water extract.

As I will show you, it is possible to prepare two tubes, one containing luciferin solution, and quite dark, the other containing luciferase solution and also dark, which will give a bright luminescence if mixed. The glow becomes fainter and fainter and finally disappears when all the luciferin has been oxidized.

The fourth step is our realization that the oxidation product of luciferin, which I have called oxyluciferin, can be reduced to luciferin again. I had frequently observed that solutions of perfectly dark luciferase, which, from mode of preparation must contain also oxyluciferin, were capable of giving off more light after standing for a few days. In 1918, I found that this was due to reduction of the oxyluciferin by bacteria,[3] whose strong reducing action is well known, growing in the solution. Many means of reduction of oxyluciferin are possible, involving the use of well-known reducing agents.

No one knows the exact chemical composition of these two photogenic substances. Luciferin has many properties in com-

[3] Not luminous bacteria but other kinds.

mon with the proteoses and peptones and may be considered intermediate between these two groups. Luciferase has the properties of an albumin and is an albumin, or so closely bound with albumin, that the two cannot be separated. All those who have worked with enzymes know the difficulties of their purification.

Although we cannot write a structural formula for luciferin I will point out what I believe is the essential change taking place during reduction and oxidation, namely, a hydrogenation and dehydrogenation, thus:

$$\text{Luciferin} + \text{oxygen} = \text{oxyluciferin} + \text{water}.$$

or, symbolically,

$$LH_2 + O = L + H_2O.$$

When oxyluciferin is reduced under the influence of reducing agents we have—

$$L + H_2 = LH_2.$$

The luciferin is thus regenerated. I find that reduction may be brought about by hydrogen sulphide or other sulphides, by the action of acids or alkalies on metals, whereby nascent hydrogen is produced, by palladium and sodium hypophosphite, and by reducing enzymes. My usual procedure was to add the reducing agents to a solution of oxyluciferin made by thoroughly boiling an extract of *Cypridina* in order to destroy the luciferase and oxidize all the luciferin to oxyluciferin. After allowing the oxyluciferin solution to stand for some time in contact with reducing agent, the presence of luciferin could be detected by adding luciferase solution and noting if any light occurred. If anyone doubts that reduction of the oxyluciferin is really the phenomenon observed in these experiments, I think the following observations are sufficient to prove conclusively the reality of reduction.

It is a well-known fact that reduction occurs at the cathode and oxidation at the anode when an electric current is sent through a solution. If, between platinum electrodes, a current is sent through an extract of *Cypridina* containing luciferase and oxyluciferin and some NaCl, to make it a good conductor, a beautiful luminescence appears over the surface of the cathode, none over the anode. With *n* NaCl, the luminescence is just visible at 1.8 volts across the electrodes and is marked at 2 volts. This is about

the potential at which hydrogen first appears in an *n* NaCl solution and is very slowly liberated as bubbles from the electrode.

The explanation of this experiment is as follows: Nascent hydrogen is liberated through decomposition of water by the Na set free at the cathode.

$$Na + HOH = NaOH + H.$$

The nascent hydrogen, H, reduces the oxyluciferin to luciferin, which then oxidizes with luminescence in contact with luciferase and oxygen, also present in the solution. Thus we have a layer of luciferin formed in immediate contact with the electrode and just beyond this, the oxidation of the luciferin to oxyluciferin with luminescence. By the use of oxyluciferin solution containing luciferase and oxygen we have a means of immediately determining that reduction of the oxyluciferin has occurred, which is more convenient and rapid than former methods in which I first reduced an oxyluciferin solution in absence of oxygen and then mixed it with luciferase solution containing oxygen. The present method is especially applicable to the study of reductions at the surfaces of solids and gives us an interesting insight, as we shall see later, into the action of heterogeneous catalysts.

Not only may the luminescence under the above conditions serve as an indicator of reduction of oxyluciferin, but conversely the luminescence may serve as an indicator of nascent or atomic hydrogen. Hydrogen from a cylinder will give no luminescence whatever if bubbled in a fine stream or shaken (so as to break it up into very minute bubbles) with oxyluciferin-luciferase-oxygen solution. Only if the hydrogen is liberated in the oxyluciferin-luciferase-oxygen solution so that the hydrogen possesses its "active" qualities will luminescence occur. The "active" qualities persist only within very small distances from the surface of separation, as can be easily demonstrated by this luminescent reaction. The "active" hydrogen is no doubt atomic hydrogen which changes rapidly in the sense of the equation:

$$2\,H = H_2.$$

If oxyluciferin can be reduced at cathodes during electrolysis it should be possible to observe reduction of oxyluciferin when present in a fluid serving as the electrolyte of a voltaic cell, in which two dissimilar metals are placed. It should also be possible to

observe reduction of oxyluciferin at the surface of metals capable of liberating hydrogen from water. Both possibilities can be realized.

I find that Mg, Al, Mn, Zn, and Cd, placed in oxyluciferin-luciferase-oxygen solution, luminesce over their fresh-cut surfaces. None of these metals liberate visible hydrogen from water at room temperature except Mg, but a thin film of atomic H must be formed over their surface, which is replaced as used in reducing oxyluciferin, for the luminescence may last for some time.

We are now in a position to describe the luminescent effects at galvanic couples formed in oxyluciferin-luciferase-oxygen solution plus NaCl to render the solution a conductor and electrolyte. As I have said, if a strip of Zn or Al or Cd is placed in such a solution the metals glow spontaneously. A piece of platinum placed in the solution does not glow, but if the Zn or Al or Cd is touched to the platinum, the platinum luminesces quite brightly, with greater intensity than the Zn or Al or Cd alone. At the same time the luminescence of the Zn or Al or Cd either fades or disappears. The platinum forms the cathode of the galvanic circuit at which reduction processes occur, the oxyluciferin is reduced to luciferin in immediate contact with the platinum and then is oxidized again with luminescence by the luciferase and oxygen layer next to it.

It is also possible to reduce oxyluciferin in presence of molecular hydrogen providing that a catalyst is present. As is well known, there are two groups of catalysts used in hydrogenation processes in the industries, namely, the Pt group and the Ni group.

Palladium and platinum are active examples of these. A palladinized or platinized surface, if saturated with hydrogen and then placed in oxyluciferin-luciferase-oxygen solution will glow beautifully. No luminesence appears if the Pd or Pt surface is first exposed to oxygen and then placed in the above solution.

A continuous luminescence appears if hydrogen from a cylinder is bubbled through an oxyluciferin-luciferase solution which contains palladinized gauze or colloidal Pd or Pt. It is not necessary that the hydrogen be produced in the atomic or nascent condition in contact with the metal catalysts. Molecular hydrogen in contact with Pd or Pt is converted into the active state as is evidenced by the luminescence in the above-mentioned experiment.

We may, therefore, conclude that the reason palladium acts as a catalyst is because of its power to convert molecular into nascent atomic hydrogen.

It may perhaps be emphasized in passing that we have here a means of producing a luminescent lamp which would burn for an indefinite time,[4] provided a slow stream of hydrogen and oxygen be supplied. A large palladinized surface would continually reduce oxyluciferin which would just as continually reoxidize with luminescence in presence of luciferase and oxygen. In actual practice the light produced in this way is too weak for purposes of illumination. It is a mere scientific curiosity at the present time, but I believe the principle involved an important one. Suppose we could find a substance which produced a bright light during oxidation and which was readily reducible, as oxyluciferin is. The material could be used over and over again. It would be equivalent to burning oil in a lamp and then reducing the oxidation products of the oil, the CO_2 and H_2O to oil again. A procedure not possible in the case of oil, surely, but worth considering in connection with some chemiluminescent materials.

Let me recall again to your minds the distinction between the luminous bacteria and fungi which glow continuously day and night, and the animal organisms which glow only on stimulation. Most students of bioluminescence have supposed that luciferin is continually being formed from some simpler substance as it is oxidized with light production. We may quite logically believe that the bacteria and fungi oxidize luciferin in one part of the cell and reduce oxyluciferin in another, while the animal organisms oxidize luciferin during the flash and reduce it between flashes. Should this be true, and it is not proven as yet, living processes would present a marvel of economy quite at variance with the prodigality we are apt to associate with reproductive nature.

Another phase of this work in which I have been much interested recently is a determination of the factors which control the intensity of the light. A student of mine, Dr. W. R. Amberson, has been working on this problem and has succeeded in measuring the light intensity in a test tube of solution whose luminescence gradually fades. What we wish to determine is the curve of this luminescence intensity against time, or the decay curve, to see

[4] Unless secondary reactions appear which interfere with oxidation and reduction.

upon what factors intensity depends. The problem is a difficult one but he has solved it by means of a photographic method. He has photographed the light on a moving picture film wrapped on the drum of an ordinary kymograph such as is used in physiology laboratories. The container for the luminescent mixture is a tube of glass, covered with black paint and adjusted very near the drum. On one side is a small slit, through which the light produced can shine directly on the film. A stirring device and thermometer are also placed in the tube. With two such tubes it is possible to take two records at the same time on the same moving picture film. A calibration record must also be placed on the same film. If we take records in this way during revolution of the drum, we get a streak of blackening on development which gradually fades out as the film revolves and the luminescence becomes less intense. The calibration exposures are made in order to determine how much blackening a given intensity of light will produce on the film. They are obtained by allowing the same luminescence to pass through neutral filters of known absorption before striking the film and must be impressed after the moving record is taken.

Doctor Amberson has studied the effect of changing the (1) concentration of luciferin, (2) concentration of luciferase, and (3) temperature. Oxygen is always present in such high concentration that it does not affect the light intensity even though its concentration may vary somewhat during the course of the reaction. The curves obtained are always straight lines if we plot log intensity of luminescence against time. This is just the result we should expect, if the oxidation of luciferin represents a monomolecular reaction, whose reaction velocity determines light intensity, and is presented as proof that reaction velocity does determine light intensity, within, of course, certain limits.

The luminescence intensity (reaction velocity) is about proportional to the concentration of luciferase and to the concentration of luciferin (presumably) and doubles or trebles for a rise of temperature of 10° C. There is an interesting initial flash of greater intensity than we should predict from theory lasting one or two seconds. This flash suggests conditions obtaining in a heterogeneous system but I cannot take the time to discuss this matter now.

You may be interested in some work that has been done upon the physical nature of animal light, that is largely due to Ives and Coblentz. In a photograph showing the spectrum of the light of a fire-fly, compared with the helium spectrum and the carbon incandescent light spectrum, the fire-fly spectrum occupies only a small region centred in the yellow and is not crossed by any dark or light bands or lines. You have probably noticed that some fire-flies have different luminescent color from others. Some flash with a deeper red than others. These differences in the color of the light are due to real spectral differences in the lights themselves and are not subjective illusions of our own eyes.

Some fire-flies actually possess lights of two different colors on different parts of the body and it is true that the spectra of all luminescent organisms differ somewhat. The form that I have been working with, *Cypridina*, is very different from the fire-fly. It has a very blue light but its spectrum extends over quite a range of wave-lengths. There are no infra-red and no ultra-violet rays emitted by luminous animals. There are also no penetrating radiations of any kind.

Since all radiation is in the visible, the luminous efficiency is very high, whereas in an incandescent lamp, so much of the radiation is in the infra-red that the luminous efficiency is very low. We must always remember, however, that animal light is in no way different from any other kind of light. It can be refracted and reflected and polarized, will affect the photographic plate, cause decomposition of CO_2 in presence of chlorophyll and show all the phenomena which ordinary light of the same wave-lengths exhibits.

Finally we may inquire as to the actual intensity of these lights. Everyone knows that the actual candlepower of the fire-fly is very low indeed. It is a little difficult to measure accurately, but Coblentz estimates that the flash of the fire-fly might vary from 1/400 to 1/250, and Pickering states that it has an intensity of about 1/250 candlepower, so that these candlepowers are not to be compared with the light we use to-day for illumination. However, the important fact is not the candlepower but the candlepower per area that gives off the light; what we call the intrinsic brilliancy of the light. Ives has measured it, in the case of the glowworm, which is easier to measure, as perhaps you know, the flash of the glowworm lasts a great deal longer than that of the fire-fly. He

found that the luminescence possessed an intrinsic brilliancy of .0144 lumen per square centimetre. From that we can calculate how large an area of this intrinsic brilliancy on the ceiling would be necessary to illuminate a table underneath. To properly illuminate this table, if the table is a metre high and the whole room three metres high, it was found that a disc of light on the ceiling must be two metres in diameter. If such were the case, we could then obtain a light on the table that would be ample for reading or writing or drawing. If it is possible to copy the fire-flies process you see it may not be entirely out of the question to use such light for illuminating purposes. The modern tendency of indirect lighting is to use a diffused light rather than the highly concentrated lights of enormous intrinsic brilliancy. I think it will be quite possible to reproduce the process of luminescence of living things, but whether it will be feasible to do so cheaply, commercially, is of course a question which only time can decide.

New Experiments on Photophoresis. J. MATTAUCH. (*Physikal. Zeit.*, Oct. 15, 1922.)—This name was given by Ehrenhaft to the translatory effect exerted by a concentrated beam of light upon tiny particles with electrical charges which by means of such charges are made to hover suspended between the two plates of a condenser. The particle may be moved forward in the direction along which the light passes (light-positive) or backward against the beam (light-negative). According to Maxwell's theory there would be a pressure produced by light only in the forward direction. Laski and Zerner have, however, developed a theory of photophoresis according to which the direction of the motion depends upon the location of the point of maximum temperature in the hovering sphere.

Most of the experiments were conducted with particles of selenium which has at least two modifications reproducible at will. The first variety was red and the time required for them to fall through a given distance did not change as time went on. This indicates that there was little or no evaporation. All the spheres having a radius greater than 17×10^{-6} cm. were light-positive. Those with radii from this down to 10×10^{-6} cm. were light-negative. With smaller spheres no effect was discernible. At the other end of the scale of sizes the light-positive effect went on increasing as the radius grew.

With the second, the white, form of selenium, the time of fall varies in such a manner as to show that the substance evaporates. All spheres independent of their size were light-negative, but there was a maximum effect at a certain radius. There are similarly two modifications of sulphur which in general comport themselves like the red and the white varieties of selenium so far as photophoresis is concerned. G. F. S.

CHEMISTRY OF THE ACID FIXING BATH.*

BY

S. E. SHEPPARD, FELIX A. ELLIOTT and S. S. SWEET.

THE acid fixing bath, now so general for both negative and positive processes, represents an interesting compromise between certain practical requirements, and limiting physico-chemical equilibrium conditions. This may perhaps be best exhibited by first tabulating the constituents and their respective functions, and then discussing in some detail how the exercise of these functions is governed by specific physico-chemical factors.

TABLE I.

General Composition of Acid Fixing Bath.

No.	Constituent.	Function.	Formula, etc.
1	Hypo	Fixing agent proper, dissolving silver halide	$Na_2S_2O_3.5H_2O$
2	Acid	Clearing agent, promotes swelling and increases speed of fixing, reduces stain and coloration, and is necessary to regulate hardening agent (4)	H_2SO_3 (sulphurous) or organic acid (see later)
3	Sulphite	Protects hypo against decomposition by acid. Antoxidant and anti-stain	Na_2SO_3 $Na_2S_2O_5$ (meta-bisulphite)
4	Alum	Hardens gelatin, preventing frilling, softening, etc.	Potash alum K_2SO_4, $Al_2(SO_4)_3$ Chrome alum K_2SO_4, $Cr_2(SO_4)_3$
5	Water	Solvent	H_2O

Considering now the physical chemistry of each agent and function, respectively: With regard to "hypo" and fixation proper there is not much to note. The solution of the residual silver halide after development depends primarily upon the for-

* Communicated by Dr. C. E. K. Mees, Director of Research Laboratory and Associate Editor of this JOURNAL. Published as communication No. 175 from the Research Laboratory of the Eastman Kodak Company.

mation of complex double salts. It should be noted that many double salts, or molecular addition compounds, may exist in the solid state, which give practically no evidence of combination in solution. The alums approach this condition. In general, there exists a wide range of such bodies, from such in which the dissociation into the simpler component molecules and ions is almost complete, to such giving very stable complex ions. The Abegg-Bödlander theory of electro-affinity regards such complex ions as formed by the union of simple ions with neutral molecules. Such complex ions may be regarded as transitional to colloids, particles in which we have a great number of neutral molecules stabilized by the adsorption of simple ions.

In terms of the double salt nomenclature, the solution of a silver halide, say AgBr, by thiosulphate, is represented by the equations:

(1) $2\,AgBr + Na_2S_2O_3 = 2\,NaBr + Ag_2S_2O_3$
Silver thiosulphate

(2) $Ag_2S_2O_3 + Na_2S_2O_3 = Ag_2S_2O_3.Na_2S_2O_3$
Silver monosodium thiosulphate

(3) $Ag_2S_2O_3.Na_2S_2O_3 + Na_2S_2O_3 = Ag_2S_2O_3.2\,Na_2S_2O_3$
Silver disodium thiosulphate

or in terms of the reacting ions, and indicating the reversibility of the reactions

(1a) $\overset{+}{Ag} + \overset{=}{S_2O_3} \rightleftarrows AgS_2O_3^-$

(1b) $AgS_2O_3^- + \overset{=}{S_2O_3} \rightleftarrows Ag(S_2O_3)_2^{=}$

(1c) $Ag(S_2O_3)_2^{=} + \overset{=}{S_2O_3} \rightleftarrows Ag(S_2O_3)_3^{\equiv}$

For a given silver halide, the ultimate or basic condition for the efficiency of a fixing bath is the stability of the silver complex ion formed. Thus the stability of the complex $Ag\overline{S}_2O_3$ is measured by the value of the expression:

$$\frac{\left[\overset{+}{Ag}\right]\left[\overset{=}{S_2O_3}\right]}{\left[Ag\overline{S}_2O_3\right]} = K$$

where the square brackets indicate concentrations. These "complexity constants" may be determined in various ways experimentally.[1] Further, from the form of the expression it will be seen

[1] Jacques, "Complex Ions," Longmans, Green and Company, London.

that K is proportional to the concentration of silver cations. Now this will be determined by the solubility product of the silver salt.

For $\overset{+}{Ag} + \overset{-}{Hal} \rightleftarrows AgHal$ we have in the presence of solid halide

$$\left[\overset{+}{Ag}\right]\left[\overset{-}{Hal}\right] = \text{const.} = \text{solubility product}$$

Hence, the *less* soluble the given salt is in water, the higher must be the stability of the complex ion formed to ensure complete solution. Thus potassium or sodium cyanide is necessary to dissolve silver sulphide, Ag_2S, the least soluble of silver compounds, and it will be seen from the following table that the complex silver cyanidion is the most stable:

TABLE II.

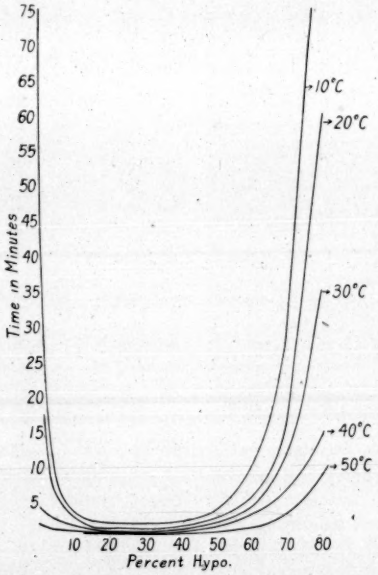
Formula of Silver Complex Ion.	Condition Electric.	Conc'n Limit of Free Anion.	K.
$Ag(\overline{S_2O_3})_2$	anion	below .1 N	$.98 \times 10^{13}$
$Ag(\overline{S_2O_3})_3$	anion	above .5 N	3.45×10^{13}
$Ag(\overline{CN})_2$	anion	under .05 N	$.11 \times 10^{21}$
Ag_2I_4 to AgI_4	anion	indefinite	7.7×10^{13}
$Ag(\overline{CNS})_2$	anion	below .2 N	6×10^{9}
$Ag(\overline{CNS})_3$	anion	above .3 N	1.5×10^{9}
$Ag(\overset{+}{N}H_3)_2$	cation		$.15 \times 10^{8}$

These are the fundamental equilibrium values determining the ultimate efficiency and economy of a fixing solution. The rate of fixation is, however, greatly affected by quite other considerations than these conditions of chemical equilibrium. It was shown by Sheppard and Mees [2] that for relatively dilute solutions of "hypo," up to 5 per cent. the rate of fixation is directly proportional to the concentration of the "hypo," and gives, over a considerable range, a linear function of the time. Further, it was shown that the speed of fixation depends greatly upon stirring. It was concluded from these results that the speed of fixation is primarily determined by the rate of interchange of the soluble components between the film and the solution, and principally by the diffusion out of the complex ion.

[2] "Investigations," p. 113 *et seq.*

These experiments were made for concentrations lower than those used in practice, and bear on the *rate*, rather than the total time of fixation, which chiefly concerns the photographer. A valuable series of investigations on the integral time of fixation—or better, the semi-total time—was described by Welborne Piper.[3] As a criterion for the "time of disappearance" he used a streak

FIG. 1.



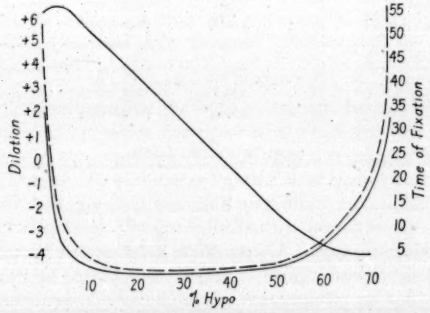
of hypo solution made across the plate before immersion, the "time of fixation" being the time for this to vanish. He found that an optimum concentration of "hypo" existed, giving the least time of fixation, at ordinary temperatures, between 30 and 40 per cent. Fig. 1 shows curves for experiments made by us on Seed process plates kept in motion during fixation.

In a general way the data confirm Piper's results. They show

[3] *B. J.*, p. 59, 1913.

that the influence of temperature is a pronounced function of the concentration. Increase of temperature has evidently a double influence, increasing the rate of diffusion, and also increasing the swelling of the gelatin. The values at 40° and 50° C. for low concentrations of hypo indicate that swelling is passing here into solution. The existence of an optimum concentration (for least time of fixation) appears to be due to the point of balance between increase of diffusion velocity with concentration, and decrease of swelling of gelatin with concentration of the saline hypo solution.

FIG. 2.



Outside curves show time of fixation, inside (linear) curve swelling compared with water.

STRATO-CHEMICAL FACTORS.

When a reaction can proceed with different velocities, and often to different apparent equilibria at different depths in a system little susceptible of internal mixing by convection, we encounter a variety of phenomena conveniently termed "strato-chemical." From the evident importance of the osmotic interchange between outer solution and the gelatin film in fixation we should expect strato-chemical factors to be of importance. Thus the integral time of fixation is mainly determined by the reaction-time of the lowest layer, adjacent to the support. Not only does the thickness of the film play a great part, but the position of the plate, particularly at rest. Thus we find a great difference in time of fixation between plates fixed at rest, in a horizontal position, according as the gelatin emulsion side is upmost or down-

most. In fact, a plate fixing at rest, but with gravity assisting the removal of the reaction-products, does not lag far behind one kept in movement. It seems probable that the gravitational down-flow of the heavier complex compounds tends to produce a local current at the plate surface. Two examples will suffice to illustrate this.

TABLE III.

Plate.	Per cent. Hypo.	Time of Fixation—Secs.	Position.	Ratio.
Seed 23	16	523.0	face up	2.3
	16	227.0	face down	
	16	183.0	in motion	
	32	126.0	face up	1.62
	32	139.3	face down	
	32	109.0	in motion	

ACID IN FIXING BATH.

The acid fixing bath was introduced by A. Lainer in 1889, with the object of combining the acid clearing bath frequently used after development with alkaline organic developers to remove yellow oxidation stain. Using dilute solutions of various acids, as sulphuric, formic, tartaric, acetic and citric, he found that milkiness due to precipitation of sulphur could be overcome by combining the acid first with sodium bisulphite solution and adding this to the thiosulphate.[4] Under these conditions, provided the acid is not too strong, the solution remains clear and does not deposit sulphur. Instead of tartaric or citric acids, metabisulphite may be used.

Lainer's theory of the acid fixing bath based on preferential decomposition of the sulphite, and assumed formation of acid salts does not appear adequate. A more satisfactory explanation is derived from certain independent investigations on the physical chemistry of the decomposition of thiosulphates by acids. H. Landolt,[5] in a paper on the "Time of Existence of Thiosulphuric Acid in Aqueous Solutions," reached the following conclusions: (i) The nature of the acid employed does not affect the decomposition; (ii) the time of stability is independent of excess of

[4] *Phot. Corresp.*, 1889.
[5] *Ber.*, **16**, 2958, 1883.

thiosulphate or of acid; (iii) it is also independent of the absolute volume of solution; (iv) the decomposition starts sooner with increased temperature, but the temperature coefficient falls with rising temperature. It is facilitated by dilution.

Landolt considered that the "life-period" of thiosulphuric acid was measured by the interval between the addition of an acid solution to thiosulphate and the first appearance of a sulphur cloud or opalescence.

This induction-period was made the subject of an extensive investigation by H. von Oettingen.[6]

Considering that all the reactions were between ions, he supposed that the actual reaction was between the thiosulphate ion and the hydrogen ion from the acid, according to the equation

$$S_2O_3^{=} + H^{+} \rightleftarrows HSO_3^{-} + S$$

According to this, neither the sodium ion nor the acid anion take part in the reaction, which explains why the nature of the acid does not affect the decomposition.[7] Oettingen's results, however, do not confirm Landolt's statement that the decomposition is independent of the concentration of the acid. He criticizes the conception of a definitive "time of existence" or "life-period" of a chemical molecule, such as thiosulphuric acid, as the cause of the induction, and regards this as due to supersaturation of the solution with sulphur. This he supposes to pass through a metastable limit before spontaneous precipitation becomes possible. Contrary to Landolt, he found the induction decidedly dependent on the concentration of acid. For hydrochloric acid the curves relating the time of induction to the hydrogen ion concentration were found to be continuous curves, representable with fair accuracy by the equation

$$T = \frac{1}{A \log(1 + bC_H)}$$

Where A and b are constants and C_H is the hydrogen ion concentration obtained from conductance measurements. The independence of the nature of the acids is limited to the conditions that isohydric solutions be used, *i.e.*, concentrations equivalent with respect to hydrogen ion. The inhibiting action of sulphite is shown by a change in the constants A and b.

[6] *Zeit. physik. Chem.*, **33**, 1, 1900.

[7] Within certain limits discussed later.

EQUILIBRIUM CONDITIONS.

This action of sulphite is discussed by v. Oettingen from the point of view that the reaction

$$\overset{=}{S_2O_3} + \overset{+}{H} \rightleftarrows H\bar{S}O_3 + S$$

is reversible, so that the action of sulphite is due to mass action of the sulphite in increasing the reverse reaction. Qualitatively this agrees with the production of thiosulphate from sulphite and sulphur. Experiments by Colefax [8] to determine the equilibrium showed that disturbing side reactions occur, *e.g.*,

$$2\,Na_2S_2O_3 + 3\,SO_2 = 2\,Na_2S_2O_6 + S$$

Foussereau [9] followed the decomposition by conductivity measurements. The curves, with times as abscissæ and change of conductance as ordinate, show that with dilute mixtures of thiosulphate and acid the curves show decided inflection. This he attributed to supersaturation of sulphur, and autocatalysis by primary sulphur nuclei. He confirmed this by abbreviating the induction by the addition of partly decomposed solutions. That the reaction $H_2S_2O_3 = H_2SO_3 + S$, the decomposition of thiosulphate to sulphite and sulphur does not go quantitatively is easily shown; the iodine titration value should double for complete reaction, but actually it only increases some 80 to 85 per cent. It was shown early that small quantities of polythionates are formed [10] and Raschig [11] considers that pentathionate is first formed, according to the equation

$$\underset{\text{thiosulphate}}{5\,Na_2S_2O_3} + 3\,SO_2 = \underset{\text{pentathionate}}{2\,Na_2S_5O_6} + 3\,Na_2SO_3$$

which then reacts with sulphite according to the reactions

$$\underset{\text{pentathionate}}{2\,Na_2S_5O_6} + \underset{\text{sulphite}}{3\,Na_2SO_3} = \underset{\text{trithionate}}{Na_2S_3O_6} + \underset{\text{tetrathionate}}{Na_2S_4O_6} + \underset{\text{thiosulphate}}{3\,Na_2S_2O_3}$$

so that the net result is given by

$$\underset{\text{thiosulphate}}{2\,Na_2S_2O_3} + 3\,SO_2 = \underset{\text{trithionate}}{Na_2S_3O_6} + \underset{\text{tetrathionate}}{Na_2S_4O_6}$$

[8] *Trans. Chem. Soc.*, **61**, 176, 199 (1892).
[9] *Ann. Chim. Phys.*, **15**, 533 (1888).
[10] G. Chancel and E. Deacon, *J. prakt. Chem.*, **90**, 55 (1863).
[11] *Zeit. angewandte Chemie*, **33**, 261 (1920).

An interesting case of chemical induction was discovered by Salzer [12] in connection with this. If a trace of potassium or sodium arsenite be added to thiosulphate before addition of acid, the decomposition into sulphurous acid and sulphur is largely inhibited, practically the whole of the thiosulphate becoming converted to polythionate. Soluble arsenates may also be used. This reaction has no actual value for the acid fixing bath, since although precipitation of sulphur is prevented, thiosulphate is actually rapidly removed. Hence it is rather the exclusion of arsenic, as an impurity, which is desirable. It appears then that in any case the influence of sulphite is due to its action as a product of a reversible reaction. Probably, however, colloid chemical considerations come into play in determining the rate of precipitation of sulphur, namely, the influence of the electrolytes present on the stability and coagulation of the sulphur hydrosol.

CONTROL OF HYDROGEN ION CONCENTRATION.

It is evident that, for a given quantity of protecting sulphite—a quantity which it is not desirable to exceed both from economic considerations, and from the fact that such excess will slow fixation by repressing swelling of the gelatin—there will be an upper limit to the permissible H-ion concentration, beyond which the protective action would exhaust too rapidly. This exhaustion or decline of the protective effect is due to more or less gradual volatilization of sulphurous acid, as well as oxidation of the sulphite. On the other hand, the concentration of H-ion must be *above* a certain lower limit, in order that the bath may be truly an acid fixing bath. The clearing action of acid on stains is primarily due to conversion of colored salts of dyes into colorless acids; while for definite known dyes the value of H-ion necessary can be specified,[13] the products of developer oxidation are too indefinite for this. In the presence of sulphite as well there is possible also a specific bleaching action of sulphurous acid. A further necessity for a definite lower limit of H-ion is introduced by the alum. The hardening action of this is connected with hydrolysis in the gelatin, with retention of colloidal alumina. If the reaction is too alkaline the penetration of the alum is insufficient, and also the solution becomes unstable. Further, if as frequently happens, the

[12] *Chem. Ber.*, 19, 1696 (1886).

[13] *Cf.* W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore.

alum is contaminated with iron, this *iron* will react with the polyphenolic bodies coming over from the developer, producing dark inky colorations. This effect is prevented by an acidity corresponding to $p_H \leqq 6.0$. This is another instance of the influence of iron, as an impurity, upon the chemistry of photographic processes.[14] The acidity must be sufficient to neutralize alkali from developer left in the film after rinsing with water. There is not only liability of the organic reducer to autoxidation, but by acting on the complex silver solution produced by the thiosulphite either actual intensification of the image may be produced, or colloidal silver deposited as dichroic fog.

For physical chemical purposes it is most convenient to express the hydrogen ion concentration as a logarithmic function. The value p_H, introduced by Sörensen as the exponent of the hydrogen ion concentration,[15] is given by

$$p_H = \log \frac{1}{\left[\overset{+}{\mathrm{H}}\right]}$$

when $\left[\overset{+}{\mathrm{H}}\right]$ is the concentration of hydrogen ion. The p_H value may be measured directly as the electrode potential of a hydrogen electrode immersed in a given solution [16] or colorimetrically. We have determined the practically permissible limits of p_H in acid fixing baths, both in the absence and in the presence of alums and hardeners. It is necessary to consider here the interaction of the bath with gelatin, but before doing this we must notice the question of *reserve* acidity.

RESERVE ACIDITY OF FIXING BATHS.

The undissociated part of an acid furnishing H-ion according to the equilibrium

$$\mathrm{H\,An} \rightleftarrows \overset{+}{\mathrm{H}} + \bar{\mathrm{A}}\mathrm{n}$$

where $\bar{\mathrm{A}}\mathrm{n}$ is an anion, is the " reserve acidity " which is called into action as fast as the equilibrium is disturbed by removal of the dissociation products. The neutralization of entrained alkaline developer in film, plate or paper will evidently remove H-ion.

[14] *Cf.* S. E. Sheppard, " Effect of Iron Content of Ammonium Persulphate." *Brit. J. Phot.*, **65**, 314 (1918).

[15] *Cf.* W. M. Clark, *op cit.*

[16] According to Nernst's equation.

Hence, in order that the concentration of this (or the p_H value) may not change seriously before the actual fixing efficiency of the bath is exhausted, the acid component should have the requisite reserve acidity. Otherwise expressed, we must be able to take sufficient total acid, but suitably regulate actual acidity or H-ion concentration, to prescribed limits.

Organic acids, as weak acids, are the most suitable for this purpose, and are easily regulated, or "buffered" by addition of a suitable amount of their sodium salts. Data of Walpole [17] illustrated how the $\left[\frac{+}{H}\right]$ varies in a solution of acetic acid and sodium acetate. Taking 10 c.c. of N/5 acetic acid, and adding various amounts of caustic soda, we have:

TABLE IV.

N/5 NaOH	Ratio $\frac{\text{Salt}}{\text{Acid}}$	p_H
c.c.		
0.20	0.020	3.08
0.50	0.053	3.42
1.0	0.111	3.72
2.0	0.250	4.05
3.0	0.429	4.27
4.0	0.667	4.45
5.0	1.000	4.63
6.0	1.500	4.80
7.0	2.33	4.99
8.0	4.00	5.23
9.0	9.00	5.57

HARDENING ACTION OF ALUM ON GELATIN.

Hardening agents for gelatin may be divided into temporary and permanent hardeners. A temporary hardener acts simply by repressing swelling; concentrated solutions of many neutral salts, *e.g.*, of sodium sulphate, alone or in presence of acid, operate in this way. Since a concentrated jelly melts at a higher temperature than a more dilute one,[18] hardening is secured for the duration of these conditions, but is readily reversed by soaking in water. Permanent hardening, which is of a similar character to the tanning of leather, is not simply reversed, and involves fixation of other substances by the gelatin. The question as to whether the fixation

[17] *Cf.* W. M. Clark, "Determination of Hydrogen Ions," p. 17.

[18] *Cf.* S. E. Sheppard and S. S. Sweet, *J. Ind. Eng. Chem.*, 13, 423 (1921).

of aluminium, chromium and iron compounds by gelatin is due to chemical combination, or to adsorption,[19] has been much debated. Without endeavoring to settle this forthwith, we must notice that recent work[20] has shown that the reactivity of the amphoteric gelatin is markedly dependent upon the hydrogen ion concentration of the solution with which it is in equilibrium. Broadly stated, it appears that for $p_H > 4.7 - 4.8$ the isoelectric point, gelatin is a cation, and combines with anions, for $p_H < 4.7 - 4.8$, gelatin forms anions, combining with cations.[21] At the neutral, or isoelectric point, it is in its least reactive condition. From this, we should expect that gelatin would combine with $\ddot{A}l$-cation for $p_H > 4.8$ and in fact Loeb[22] has given some data on the effect of $AlCl_3$ on gelatin solution supporting this view. The evidence, however, appears to us inadequate, because Loeb used solutions of steadily *decreasing* concentration of $AlCl_3$, and simultaneously *increasing* H-ion. Deductions from experiments with such a complication seems questionable. Our own experiments on the hardening of gelatin by aluminium, etc., solutions, show the matter to be more complicated. The state of the aluminium in solution has itself to be taken into consideration, since aluminium hydroxide is itself an amphoteric substance. Most simply formulated, we have[23]

$$\ddot{A}l + 3\,OH' \rightleftarrows Al(OH)_3 \rightleftarrows \dot{A}lO_2 + H_2O + \dot{H}$$

from which it would follow that there is a certain hydrogen ion concentration at which hydrous alumina has the least tendency to form either $\ddot{A}l$ ions or AlO_2' anions, *i.e.*, the isoelectric point. As to the p_H value of this point, the evidence is incomplete and inconclusive. J. H. Hildebrand[24] showed that alumina is precipitated by sodium hydroxide from aluminium sulphate solution when the hydrogen ion concentration varied roughly during precipitation between 10^{-3} and 10^{-5}, *i.e.*, $p_H = 3$ to 5.

[19] See discussion by H. R. Procter, "First Report on Colloid Chemistry in its Industrial Applications," *Brit. A. A. Science*, 1917, p. 12.

[20] *Cf.* J. Loeb, "Proteins and the Theory of Colloid Behavior," New York, McGraw Hill Co., 1922.

[21] Where dyes and amphoteric compounds are in question, this statement requires qualification.

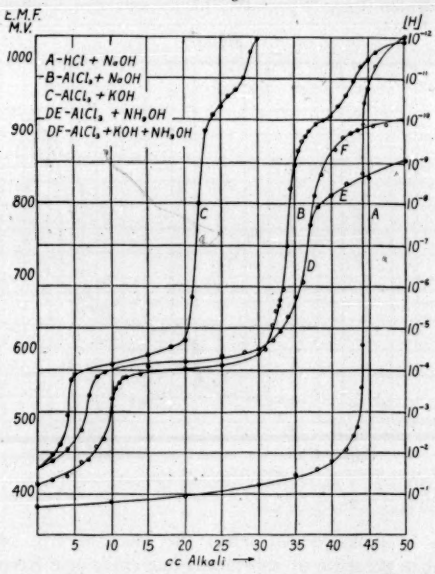
[22] *J. Gen. Physiolog.*, I, 503 (1919).

[23] J. Stieglitz, "Elements of Qualitative Analysis," p. 171 (1911).

[24] *J. Am. Chem. Soc.*, 35, 24 (1913).

The work of Blum[25] on the reactions of aluminium compounds with certain bases led to somewhat greater precision. His data on the changes in hydrogen ion concentration occurring on addition of alkalies to $AlCl_3$ solutions are reproduced graphi-

FIG. 3.



(From Blum.)

cally in Fig. 3. From these it appears that the course is largely independent of the alkali used; in general, precipitation[26] begins when $p_H = 3$, and is complete before $p_H = 7$.

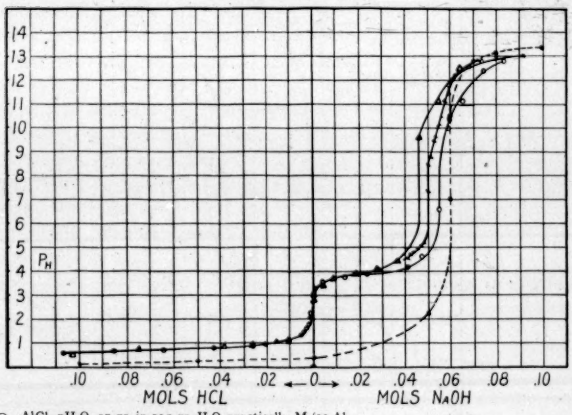
Now we have made up hardening solutions from alum ($K_2Al_2(SO_4)_4\ 24\ H_2O$) in which, first, the acidity (H-ion) was varied

[25] *J. Am. Chem. Soc.*, **35** (1913); *Sci. Pap. Bur. Stand.*, No. 286 (1916); *J. Amer. Chem. Soc.*, **38** (1916).

[26] By this Blum states that chemical formation of $Al(OH)_3$ is meant, not necessarily visible coagulation, which is variable, and may not occur until one-third to one-half the alkali for complete precipitation has been added.

by addition of acid (HCl) and alkali (NaOH), respectively; p_H measurements were made electrometrically, and the curves plotted (Fig. 4). Some differences from Blum's curves for $AlCl_3$ and bases exist, but not large, and partly accountable if the samples of $AlCl_3$ and Al_2SO_4 used had slightly different free acid contents. But also there is probably an influence of the anion. This

FIG. 4.



○ $AlCl_3.xH_2O$ .57 gr. in 105 gr. H_2O practically M/10 Al.
△ $Al_2(SO_4)_3.xH_2O$ .57 gr. in 105.98 gr. H_2O practically M/10 Al.
× $Al_2(SO_4)_3.xH_2O$ .57 gr. in 105.98 gr. H_2O practically M/10 Al (this solution stirred).
● .6M HCl, the equivalent of the Al salt.

conclusion is strengthened when the electrometric titration is carried out in presence of substances like *citric acid* having strong complex-forming tendency with alumina.

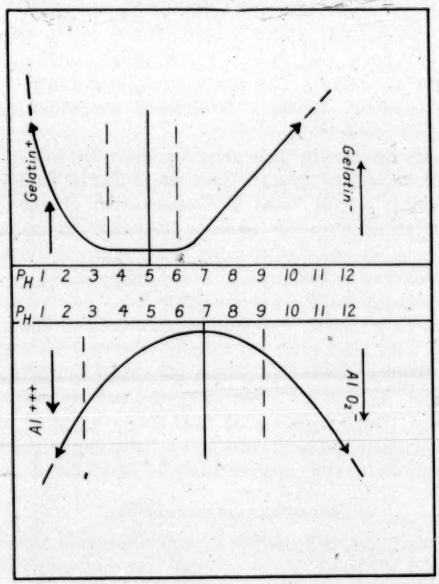
It is probable that the neutral complex is not simple $Al(OH)_3$, in these cases, but so-called basic salts. Even in the case of $AlCl_3$ and NaOH Wo. Pauli [27] has found evidence that the sols of "colloid" alumina, prepared by hydrolysis of aluminium salts, may be regarded as aggregates of intermediate complex ions, following the transition:

$$Al(OH)Cl_2;\ Al(OH)_2Cl;\ 2\,Al(OH)_3.Al(OH)_2.Cl$$

[27] *Cf.* "Physics and Chemistry of Colloids" (report of general discussion at Faraday Society), published by Department of Scientific and Industrial Research, Gt. Britain, 1921, p. 16.

"In all cases the metal hydroxides show a tendency to transform themselves, by the addition of an inorganic molecule, into charged particles, an aggregation of which forms the colloid complex" . . . "with increasing concentration of $Al(OH)_3$, the aluminium oxy-salts incline to the formation of *negative* aluminate complexes, in addition to the positive ones. This tendency in-

FIG. 5.



creases with increasing dilution, so that certain aluminium hydroxide sols stand at the boundary between positive and negative colloids." In this connection the discussion by C. Blomberg [28] of cases of complex ionization with two complex ions is of interest. Magnesium citrate, calcium citrate, show few if any ions of the metal. Similarly aluminium precipitation as Al_2O_3,xH_2O

[28] *Zeit. f. Elektrochem.*, 21, 437 (1915).

is prevented by citrates, as also its alizarine lake formation. We have, therefore, as probable primary ionization

$$Mg_3Ci_2 \rightleftarrows (Mg_2Ci)\cdot + (MgCi)'$$

and secondarily only, dissociation of free Mg and citrate ions. Similarly with Al:

$$3\,AlCi \rightleftarrows (Al_2Ci)\cdot + (AlCi_2)'$$

are possible complexes, the formation of which will be helped by excess citrate ion.[29] With varying H-ion, inversely, OH-ion, neutral molecules $[Al_2\,Ci\,H]$ to $AlCi_2(OH)$ can be formed, and this may explain the effect of the citrate addition in displacing the p_H curve. The apparent opposite effect of sulphite and thiosulphate (curves determined colorimetrically) is less comprehensible.[30]

We may summarize these results roughly by Fig. 5. In the upper half the line at $p_H = 4.8$ gives the isoelectric value dividing electropositive gelatin from electronegatively charged gelatin. Below is the diagram for alumina. Aluminium cations exist up to $p_H = 3$, in absence of citric, etc., acid; no definite isoelectric point can be assigned on other grounds, but $p_H = 6$ to 8 seems the most probable from ionization data. Loeb states $p_H = 7$ (the point of complete precipitation, according to Blum) is the isoelectric point, but gives no definite reasons. It is apparent, from the diagram, when both gelatin and aluminium salts are present together, as well as other ionogenic and complex-forming components, that a complicated and slowly adjusted series of equilibria is likely. The formation of "aluminium gelatinates," as suggested by Loeb,[31] appears likely to be limited to a narrow p_H range.

EXPERIMENTAL HARDENING.

This conclusion is borne out by experiments on alum hardening, in which the H-ion of the solutions was measured and plotted as abscissa against *melting point* as ordinate. From Fig. 6 it will be seen that in absence of alum, the maximum *m.p.*—at 34° C.—

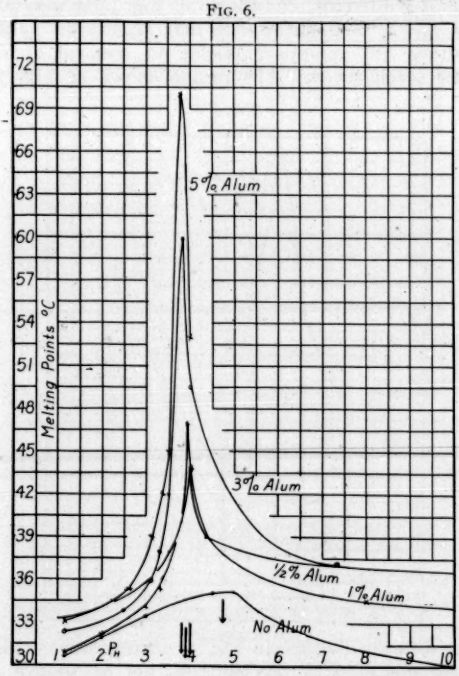
[29] These equations are suggestive only. Much work on solubilities, transport numbers, conductances, etc., is required to establish the actual conditions.

[30] The formation of aluminium thiosulphate and basic sulphites may play a part here.

[31] Loeb's diagram (*loc. cit.*) appears to be somewhat misleading, postulating a "region" of aluminium-gelatinate extending indefinitely from $p_H = 5$ to increasing values of p_H.

was at the isoelectric point of gelatin $p_H = 4.8$. With alum, and using HCl and NaOH to adjust the p_H, results expressed in Fig. 6 were obtained. The tendency is for the maximum hardening to occur near $p_H = 4.0$, but the value diminishes as the alum

FIG. 6.

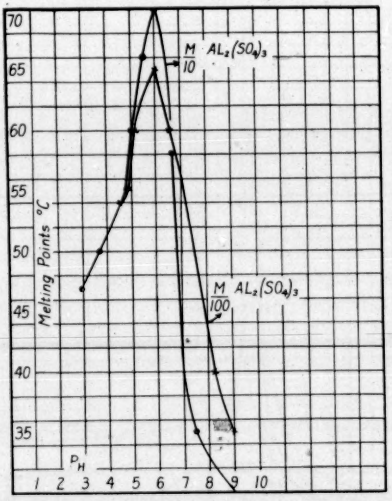


concentration is increased. From this it seems probable that the hardening is effected by $Al\cdots$, $Al(OH)\cdot\cdot$, $Al(OH)_2^{\cdot}$ ions interacting with negative gelatin ions (including such complexes as $3\,Al(OH)_2\ Al(OH)_3$). This necessitates the existence of gelatin anions at $p_H < 4.8$, but this is possible in the neighborhood of the isoelectric point.[32]

[32] The possibility that a complex aluminous *anion* is reacting with electropositive gelatin may also be considered, but is little likely.

On the other hand, if an alum salt, *e.g.*, $Al_2(SO_4)_3$, is added, with stirring, to a solution of gelatin, to which definite amounts of acid or alkali have been added previously, the dependence of the *melting point* of the jellies upon the p_H (of the jelly solution) is considerably different. As shown in Fig. 7 the maximum now occurs at $p_H = 6$, consequently we may regard the value $p_H = 4$ found before, for solutions, as due to removal of diffusible Al-ions by precipitation. The results shown in Fig. 7 are in

FIG. 7.



agreement with the diagram in Fig. 5. But positive Al-ions may be removed not only by precipitation, but by soluble complex formation, *e.g.*, with organic acids.

ORGANIC ACIDS.

As we have seen, if hypo (thiosulphate) is to be present, it is desirable to use organic acids, so that the p_H may not fall below a limit leading to sulphur precipitation. For solutions *acetic acid* is preferable, but for fixing salt powders citric acid has been much used. Taking 3 per cent. alum, the effect of different per-

centages of citric radical, or citrate ion, over a wide p_H range, is shown in Fig. 8.

It will be seen that the hardening action of aluminium salts is very rapidly decreased by increasing citric ion. In the presence of sulphite and thiosulphate, the p_H for maximum hardening is raised, and the region of hardening extended somewhat (Fig. 9).

FIG. 8.

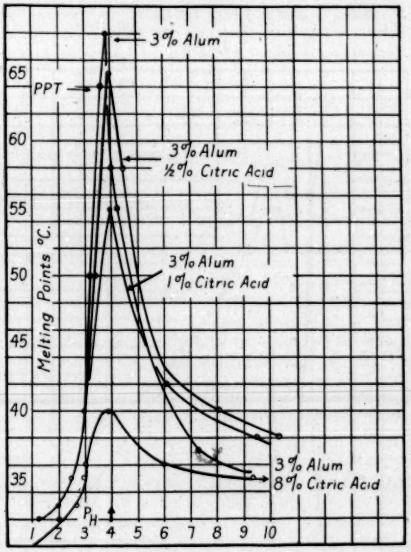


TABLE V.

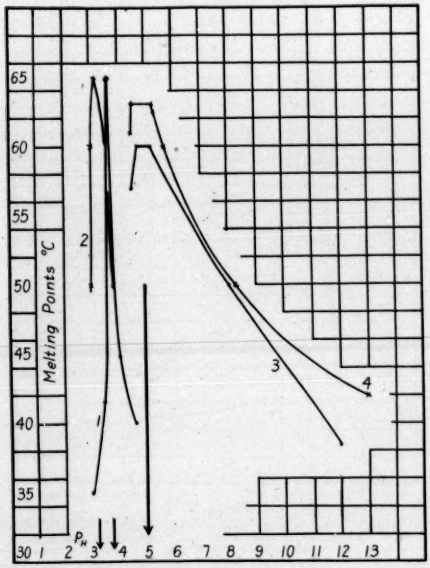
Component.	Grams per 1000 c.c.					
Hypo	240	240	240	240	240	240
Alum	8	8	8	8	8	8
Sodium bisulphite	50	50	30	30	30	30
Sodium citrate	5	5	2	5	10	20
Time of fixation in mins.	5	8	5	5	4.5	6
Melting point of emulsion ° C.	42°	37°	55°	40°	38°	35°
Precipitation	+	+	−	−	−	−

This table shows the effect of citrate ion in reducing the hardening action of aluminium on a gelatin emulsion, the melting point of which in water was about 34° C.

Investigation showed that while *formate* and *acetate* did not interfere very much, all of the following acid radicals had a similar inhibiting effect:

Oxalic	$(COOH)_2$
Lactic	$CH_3.CH.OH.COOH$
Citric	$(CH_2.COOH)_2.C(OH)COOH$
Tartaric	$COOH.(CHOH)_2.COOH$
Malic	$COOH.CH_2.CHOH.COOH$
Maleic	$COOH.CH:CH.COOH$

FIG. 9.



1. 3 per cent. alum, 0.5 per cent. citric acid, 1 per cent. Na_2SO_3
2. 3 per cent. alum, 0.5 per cent. citric acid, 2 per cent. Na_2SO_3
3. 3 per cent. alum, 0.5 per cent. citric acid, 1 per cent. Na_2SO_3, 25 per cent. $Na_2S_2O_3$
4. 3 per cent. alum, 0.5 per cent. citric acid, 2 per cent. Na_2SO_3, 25 per cent. $Na_2S_2O_3$

This action is to be attributed to the formation of complexes, as already noted. Now practically, it is necessary that the acid fixing bath have a considerable amount of organic acid, in order that the reserve acidity may take up alkali from the developer.

Again, each hardening operation removes a certain amount of alumina. *Hence, for maximum hardening the acid fixing bath should have a considerable quantity of organic acid,*[33] *and as large an amount of aluminium or chromium salt as is consistent with maintaining a* $p_H = 4$ *or slightly greater.* Acid making the $p_H = 3$ is unsafe, while acidity $p_H > 5$, while it may not precipitate alumina,[34] will give poor hardening.

The following assemblage of desiderata or specifications for an acid fixing and hardening solution shows that while the theoretical investigation can indicate the governing conditions, practically a compromise has to be effected.

1. Long fixing life,[35] that is, as high a concentration of "hypo" as possible.

[33] Or, as noted later, of sulphurous acid (bisulphite) plus salt of organic acid.

[34] Or basic aluminium salts.

[35] The limits of useful life of a fixing bath in respect to silver saturation have been investigated by Gaedicke (*Eder's Jahr.*, 1906, p. 4) and by Messrs. Lumière and Seyewetz (*Photo. J.*, **47**, 129 (1907)). The former deduced the limits from the discoloration of a test impregnated with thiosulphate, dipped in various strengths of silver nitrate, and exposed to light and air. The latter worked directly with silver bromide. They found a larger amount of silver, as bromide, could be added to thiosulphate, without decomposition, than as nitrate. Thus Gaedicke found that to a solution of 15 per cent. hypo, only 1/10 of the silver nitrate causing complete saturation can be added without permitting discoloration of the paper tint. Lumière and Seyewetz found that 60 per cent. of the silver bromide saturation can be added without producing discoloration, for 15 per cent. solution, but only 24 per cent. of that saturating a 45 per cent. hypo solution. Addition, to the 15 per cent. hypo solution, of 1.5 per cent. bisulphite lowered the limit to 27 per cent. (of saturation), while further addition of .5 per cent. chrome alum raised it again to 38 per cent. These latter results seem somewhat peculiar.

Practically, they deduce that the number of 9 × 12 cm. plates which can be fixed without fear of stain by

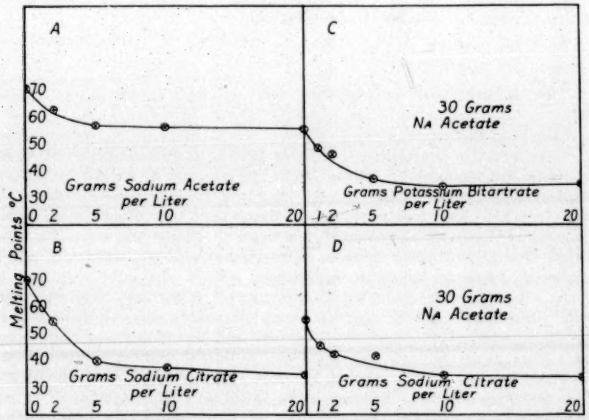
(*a*) 1 litre of 15 per cent. hypo	=	100
(*b*) 1 litre of 15 per cent. hypo	=	60
1.5 per cent. bisulphite		
(*c*) 1 litre of 15 per cent. hypo		
1.5 per cent. bisulphite	=	75
0.5 per cent. chrome alum		

Using 25 per cent. hypo this would correspond to about 15,000 sq. cms. plate or film per litre. The limit will be somewhat lower for X-ray plates, at 40 + per cent. silver halides, and higher for certain others. But approximately this works out to about 9000 sq. ins. per gallon of 25 per cent. hypo, with bisulphite, and this figure has been confirmed in this laboratory.

2. Rapid fixation hence, other things equal, "hypo" concentration should not be much above 30 per cent. Practically, the time to clear the residual silver halide should not be much more than five minutes; with a safety allowance, therefore, total time equals about ten minutes. But with strongly hardening solutions some increase in time over this is probable.

3. The bath must not deposit alumina or basic aluminium compounds, even after considerable developer alkali has been

FIG. 10.



added. This means as much organic acid radical as is otherwise compatible.

4. Since the organic acid radical must be high, small amounts of alumina will have no effective hardening action. Hence, the quantity of aluminium salt should be large.

5. The hydrogen-ion concentration should correspond approximately to a $p_H = 4$. In the presence of sulphite and thiosulphate, as will be noted, there is an apparent displacement of the p_H of maximum hardening to slightly greater p_H values. If the bath is started to have a $p_H =$ ca 3.5, it will change in the right direction as acid is neutralized and more of the "buffer" salt formed.

A bath of given "hypo" concentration, 25 or 30 per cent.

being high enough, in view of the anti-swelling action of the additional components, will fix a definite number of plates or films of given size, before becoming too saturated with silver. This limit will be reduced with increasing acidity, beyond a certain point, because of staining due to silver sulphide formation. Again, this number of plates or films will carry over a certain amount of alkaline developer and the acid reserve must be adjusted to take care of this. Further, this number will remove a certain amount of alumina, and the alum content must be adjusted to take care of this. Actually, all the conditions cannot be completely satisfied, and something has to be sacrificed, generally on the "hardening" side.

As illustrating the influence of different organic acid radicals on the hardening, the curves in Fig. 10 are given: Bitartrate; citrate; acetate.

In the bath used, 25 per cent. "hypo" is balanced with 8 per cent. potash alum, 30 per cent. $NaHSO_3$, giving sufficient acidity ($p_H = 3.1$, but buffered with sodium acetate to $p_H = 3.5$ to 3.7).

Incidentally, it may be noted that the "hardening" bath is chiefly necessary for plates and films. With the exception of some grades of bromide paper, which show an *M.P.* of about 40° to 45° C., practically all developing-out papers are hardened to withstand temperatures of 95° C. +, above boiling point for a short time. For plates and films, requiring considerable alum hardening, therefore, a high concentration of aluminium salt is necessary with sufficient complex-forming organic acid to hold up precipitation, and to maintain a hydrogen ion concentration of $p_H = 3.5$ to $p_H = 4.5$. Practically, not more than 5 per cent. of alum is desirable, and as shown, this limits the amount of citrate ion to less than 1 per cent. of the total solution.

FOR a long time the band spectrum of nitrogen has been known, but our acquaintance has been incomplete, as is shown by the discovery of three additional bands at 5075, 5018 and 4961 Ångstrom units in the Palmer Physical Laboratory, Princeton, by O. S. Duffendack (*Phys. Rev.*, Dec., 1922). G. F. S.

IN an experimental study of the scattering of homogeneous X-rays, C. W. Hewlett came upon the interesting fact that three liquids, benzene, mesitylene and octane, comport themselves in such a manner as to resemble crystals in their action upon X-rays.

G. F. S.

The Validity of Ohm's Law for Intense Electric Fields in Electrolytes. MAX WIEN. (*Physikal. Zeit.*, Oct. 15, 1922.)—The author sets himself the problem of using a field of about 100,000 volts per cm. This high value necessitates the use of a condenser discharge so that in the brief time during which the current flows, thermal and electrolytic effects may not intervene. The general plan of the investigation is the following: Let two resistances that are equal when measured by a Kohlrausch Bridge be prepared, of which one is the electrolytic resistance to be investigated and the other a comparison resistance. One of these is inserted in the circuit traversed by the discharge of the condenser and the current strength is measured. Then the other resistance replaces the first and the discharge is repeated. If the current strength is the same in the two cases the ratio of resistances of the two inserted resistances is the same at the higher field strength as at the lower when they were found to be equal, and since the comparison resistance has not changed, it is concluded that the electrolytic one also has remained unchanged. The conclusion is, "I believe that I have presented proof that Ohm's law holds within one per cent. for electrolytes up to field strengths of about 500,000 volts per cm." G. F. S.

A New Method of Determining $\frac{e}{m}$. H. BUSCH. (*Physikal. Zeit.*, Oct. 15, 1922.)—In a Braun tube a diverging beam of cathode rays falls on a fluorescing screen. Let a magnetizing coil with its axis parallel to the axis of the rays surround them. Its effect will be to twist each ray into a spiral with its axis parallel to the direction of the magnetic lines of force. All rays coming through the same point of the diaphragm will complete one turn around the spiral in the same time so that a fluorescent screen placed just where it receives the rays at that instant will show a sharp image of the diaphragm. This is true on the assumption that the rays actually diverge from the diaphragm of the tube. As a matter of fact, the point of divergence is only near to it. This is remedied by applying a rotating magnetic field to the beam before it reaches the diaphragm. This done, a sharp image of the latter can be got on the screen by varying the strength of the longitudinal magnetic field through regulation of the current in the coil. The ratio of the elementary quantity of electricity to the mass of an electron $\frac{e}{m}$ then can be calculated from three measurable quantities, current strength, distance from diaphragm to screen and the potential of the discharge. The canonical value of the ratio is 1767×10^7 electromagnetic units per gram. A series of determinations gives for the mean value 1768 instead of 1767. The method was demonstrated at the session of German physicists in Leipzig last September. It was presented as suitable for demonstration purposes and for students' use, but in addition, it seems promising as a method of exact measurement. G. F. S.

A RELATION BETWEEN THE BRIGHTNESS AND HIDING-POWER OF WHITE PAINT-PIGMENTS.*

BY

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IT is generally recognized [1] at the present time that a mere statement of the hiding-power of a white paint-pigment will not suffice to establish the excellence of the product. Any colored contamination such as dust, stain, metallic particles, etc., will increase the hiding-power at the expense of brightness. Hence, it is necessary to state the numerical values both for brightness and for hiding-power. For purposes of comparison of the hiding-powers of two different paints it is customary [2] to add sufficient mineral or bone-black to the brighter sample so as to reduce its brightness to that of the duller and then to make measurements of hiding-power. This procedure is very laborious. In view of the importance of the subject it seemed altogether worth while to seek for a possible simple relationship between the above-mentioned properties.

The procedure followed consisted simply in measuring hiding-power and brightness of a given paint. The paints were initially prepared by Mr. H. A. Gardner and consisted merely of the pigment ground in pale linseed oil—the mixture being subsequently reduced to "brushing consistency" by the addition of more oil. The relative proportions of pigment and oil are given in Table I. To these samples, very small quantities of bone-black were added and similar measurements were carried out. The cryptometer [3] was used for hiding-power measurements while the writer's colorimeter [4] was used to carry out brightness (*i.e.*, coefficient of diffuse reflection) measurements. Because of the

* Communicated by Dr. Joseph S. Ames, Associate Editor of this JOURNAL.

[1] H. A. Gardner, "Physical and Chemical Examination of Paints, etc.," 1922.

[2] J. H. Calbeck, *Proc. Am. Soc. Testing Materials*, 1922.

[3] A. H. Pfund, JOURNAL FRANKLIN INST., Nov., 1919, p. 675.

[4] A. H. Pfund, JOURNAL FRANKLIN INST., Mar., 1920, p. 371; *Proc. Am. Soc. Testing Materials*, 1920.

fluidity of the paint mixtures, the upper colorimeter plate was coated with fumed MgO, while the paint was poured into the lower plate or saucer. The brightness measurements are probably accurate to ± 1 per cent. while the hiding-power measurements may be uncertain by as much as ± 5 per cent.

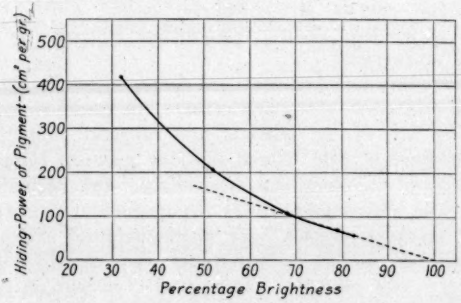
TABLE I.

Number.*	Pigment.	Percentage by Weight.	
		Pigment.	Oil.
1	Basic sulphate white lead	69.7	30.3
2	Basic carbonate white lead.....	70.4	29.6
3	Electrolytic white lead.....	71.3	28.7
4	Timonox.....	64.5	35.5
5	Zinc oxide (French process)	50.2	49.8
6	Modern process lithopone	61.6	38.4
7	Titanox	60.1	39.9

* These numbers correspond to the curves in Figs. 2 and 3.

A typical curve, covering a considerable range, both in brightness and in hiding-power, is shown in Fig. 1. This paint con-

FIG. 1.



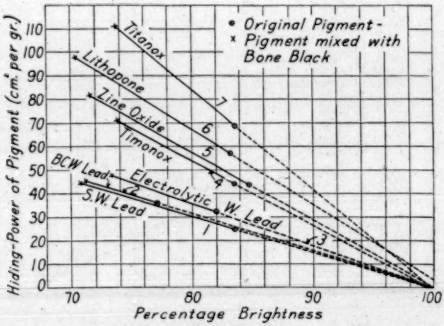
sisted of zinc oxide in linseed oil and is not included in the above list.

It is at once evident from this curve that, if we limit our considerations to that portion of the curve which lies between the brightness 70 per cent., *i.e.*, point *A*, and the terminal point *B*, the (dotted) straight line defined by these points passes through the point: zero hiding-power, 100 per cent. brightness. In order

to ascertain whether or not this relationship held for other paints also, similar tests were carried out on Gardner's paints. But two determinations were made for each paint: One, with the uncontaminated paint and the other with the grayed paint—care being taken to keep the brightness greater than 70 per cent. The results are presented in Fig. 2 and indicate clearly that, within the limits of accuracy, the relation holds quite generally.

There are several points of interest here to which attention might be called. In the first place, it is to be observed that while

FIG. 2.



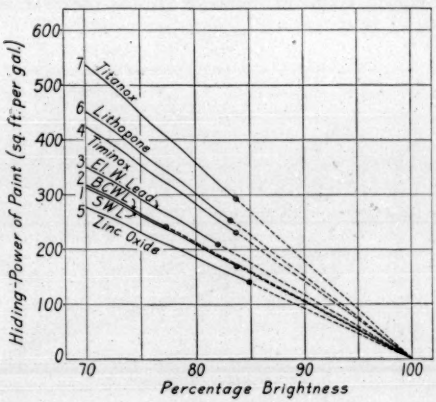
basic sulphate white lead (S.W. Lead, 1) is initially inferior in hiding-power to basic carbonate white lead (B.C.W. Lead, 2), it, *i.e.*, S.W. Lead, attains essentially the same hiding-power when its brightness is reduced to that of B.C.W. Lead.[5] Again, in the case of B.C.W. Lead (2) and Electrolytic White Lead (3) we note that, while both have the same chemical constitution, the latter is "cleaner" and has a smaller particle size. While sample (3) initially has the smaller hiding-power, it attains a higher value when the brightness is reduced to that of sample (2).

If the preceding data be recalculated so as to yield the hiding-power of the paint rather than that of the pigment, curves of the type shown in Fig. 3 are obtained. Contrasting these curves with the previous set, it is evident that the order has been changed

[5] This verifies the results of a direct comparison of these two pigments by J. H. Calbeck. *Proc. Am. Soc. Testing Materials*, 1922.

in consequence of the differences in the pigment-vehicle ratios. The point to be emphasized in this connection is that, while these curves are only approximations, they hold within the limits of accuracy of cryptometer settings. Since these curves are all essentially straight lines passing through the 0 – 100 point, it is sufficient to make but a *single brightness-hiding-power determination* at any degree of contamination (brightness greater than 70

FIG. 3.



per cent.) in order to establish the curve. This was done in plotting the curves in Fig. 3.

Such curves as these are of value, not only in making possible a comparison of hiding-powers at the same brightness, but in predicting the effect of removal or addition of contamination *so long as all other characteristics of the pigment remain unaltered.* To be specific, electrolytic white lead is essentially "clean," therefore the *extrapolated portion of the curve is meaningless.* The only manner by which the brightness of such a pigment might be increased would be to decrease the particle size. Such a change, however, would immediately result in an increase in hiding-power. This new pigment would then give rise to a new curve whose slope is steeper than that of its predecessor. (It is, of course, well known that the diminution in particle size is of advantage

only up to that point at which the particle size is of the order of the wave-length of light. A further diminution results in a decrease both in brightness and in hiding-power.)

While the extrapolated portions of the preceding curves pass through the 0 – 100 point, it is probably not true that, if a paint of 100 per cent. brightness could be realized, the hiding-power would be zero. The general form of the full curve shown in Fig. 1 would seem to indicate that the hiding-power is greater than zero at 100 per cent. brightness. This statement, however, does not affect the conclusions previously reached. It has already been pointed out that the extrapolation is meaningless beyond the point at which the pigment is "clean." The fact that the simple straight-line relation holds only for brightness values greater than 70 per cent. is no serious handicap since all modern paints, marketed as "white," have a brightness greater than 70 per cent. Any paint falling below this limit falls very definitely into the class of grays.

The curves in Fig. 2 show that a comparatively large percentage increase in hiding-power may be realized at the expense of small decrease in brightness. This point has already been alluded to in a previous paper[6] where the conclusion was reached that the *ratio* of the percentage increase in hiding-power to the percentage decrease in brightness equalled four. In light of the present work, it becomes necessary to qualify this statement more rigorously, for it is evident that this ratio is dependent upon the brightness range used in the calculations. Furthermore, this ratio decreases steadily as the brightness decreases. For infinitesimal changes in brightness, the value of the above ratio (α) is as follows:

Brightness.	α	
90%	9	(*i.e.*, the hiding-power increases, relatively, 9 per cent. as a result of decreasing the brightness, relatively, 1 per cent.)
85	5.7	
80	4.0	
75	3.0	
70	2.3	

Since all curves in Fig. 2 pass through the 0 – 100 point, these values of α apply quite generally to all white paints studied.

[6] *Proc. Am. Soc. Testing Mat.*, 1920.

(The advantage of making the initial brightness of the paint as great as possible is obvious.) If now, we make finite rather than infinitesimal changes in brightness, the value of α will depend upon the range of brightness used in the calculations. If we limit ourselves to the range within which most paints lie, *i.e.*, brightness 75 per cent. to 83 per cent., we find that, for this interval $\alpha = 5$. Possibly a more convenient form is that suggested by Dr. J. E. Booge, namely, the percentage increase in hiding-power per 1 per cent. (absolute) decrease in brightness. For the interval brightness 75 per cent. to 83 per cent. this ratio is very closely equal to 6.0. (This means that if we decrease the brightness from 80 per cent. to 79 per cent., a 6 per cent. increase in hiding-power is realized.)

The method of treating this problem, free from all uncertainty, depends upon the deduction of a formula which makes possible a calculation of the hiding-power at any brightness > 70 per cent. The curves in Figs. 2 and 3 are represented by the equation

$$y = -mx + a$$

making the following substitutions:

$y = H_B$ which is the hiding-power at any desired brightness $B > 70$ per cent.

$x = B$ which is the brightness corresponding to H_B.

$a = H_0$ which is the hiding-power at zero brightness (extrapolated).

$m = \frac{\triangle H}{\triangle B}$ which is the slope of the curve (Fig. 2 or 3)

then we have:

$$H_B = H_0 - \frac{\triangle H}{\triangle B} B$$

The operation of this formula may, perhaps, best be illustrated by citing a specific illustration: Let it be desired to calculate the hiding-power H_B of a lithopone paint (Fig. 3) reduced to the brightness 77.1 per cent. of white lead paint (curve 2). Here

$$B = 77.1$$
$$H_0 = 1502 \text{ sq. ft. per gal.}$$
$$\frac{\triangle H}{\triangle B} = 15$$
$$\therefore \quad H_B = 1502 - (15 \times 77.1) = 346 \text{ sq. ft. per gal.}$$

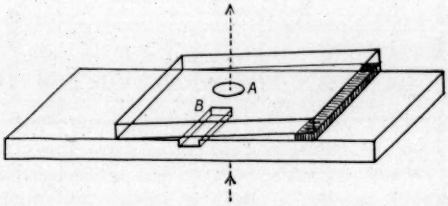
This result agrees with that obtained from the curves, directly.

It was next deemed of interest to investigate the relation between the so-called "opacity" and hiding-power. A white

pigment owes its brightness to a multiplicity of reflecting surfaces which return the incident light. As a result of such return, the intensity of the transmitted light is weakened and opacity, or better, "pseudo-absorption" develops. This may be illustrated by means of a clear piece of mica which, after having been glowed in a bunsen flame, appears almost white by reflection and black by transmission. Failure to transmit is not due to a change in the transparency of the material but to the numerous cleavage planes which now reflect the light.

In the event that all paints showed the same opacity at complete hiding, it would be possible to construct a modified

FIG. 4.



cryptometer of great sensitiveness. Anticipating subsequent results, it may be stated that these hopes were not realized. It was shown, however, that opacity, like tinctorial strength,[7] is not a quantitative measure of true hiding-power.

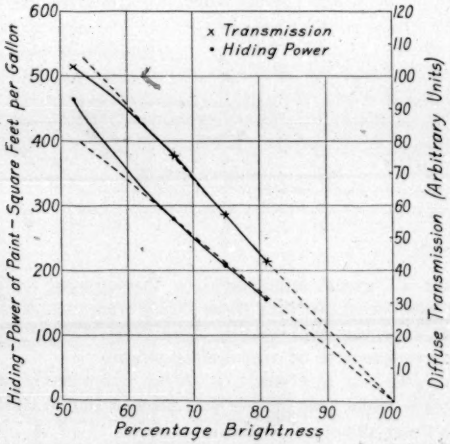
For purposes of this study, a special cryptometer was constructed. The usual deep groove was allowed to extend only half across the lower plate and a circular window *A* (Fig. 4), whose centre was in line with edge *B* was cut in the black coating covering the lower surface of the plate (made of clear plate glass). A given paint mixture was then applied to the cryptometer and the usual adjustment for disappearance of the edge *B* was made. Without disturbing this adjustment, an intense beam of white light was allowed to enter the window *A* and to pass through that portion of the paint film which had a thickness just sufficient for complete hiding. Photometric measurements of the ratio of the intensity of the emergent to the light incident upon film were subsequently carried out. The values recorded are purely

[7] Hallett, *Proc. Am. Soc. Testing Mat.*, 1922.

relative and are termed "diffuse transmissions." Obviously, they are the reciprocals of "opacities." The following curves (Fig. 5) apply to a mixture of zinc oxide and linseed oil—rubbed down with small quantities of bone-black. The brightness of these mixtures is plotted against both hiding-power and diffuse transmission.

These curves reveal the surprising result that, as bone-black is added, both *hiding-power* and *transmission increase*. In other

FIG. 5.

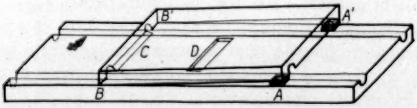


words, a film of gray paint, which is just sufficiently thick to "hide," shows greater transparency than a film of white paint which, likewise, is just sufficiently thick to "hide." Curiously enough, the straight-line extrapolation of the transmission curve also passes through the 0 – 100 point and thus allows us to draw the entirely logical conclusion that a paint showing 100 per cent. brightness is entirely opaque.

While the immediate prospects of realizing a cryptometer which would reveal very small differences in hiding-power were not realized, it was found possible to overcome a difficulty which

is met in practice when paints, containing barytes and other coarse particles, are being investigated. These coarse particles get under the areas of contact of the two cryptometer plates—hence, if the pressure on the top plate is only moderate, the coarse particles are neither crushed nor forced out and, as a result, the cryptometer reading is too low. If, on the other hand, sufficiently great pressure is exerted, the top plate is distorted and readings which are too high are obtained. Furthermore, such pressure in

FIG. 6.



conjunction with sliding motion causes a grinding action which, in time, occasions a change in the wedge-constant. These difficulties have been overcome entirely by cutting deep longitudinal grooves into both upper and lower plates (Fig. 6).

The usual metallic strip attached to the top plate is replaced by two small metallic squares at *A* and *A'*; again, the glass in the central area at *C* is cut away for a distance of 5 mm. When this plate is laid upon the lower one, contact is made only on the outer, narrow strips at *AA'* and *BB'*. Upon filling in the ends of the transverse groove, *D*, it is found that, when paint is applied to the area between the longitudinal grooves, the upper plate may be moved back and forth many times without dragging paint to the outer strips along which the plates are in contact. Needless to say, no pressure other than the weight of the top plate is now necessary. Very consistent results are obtained as a result of these modifications.

A further refinement has been introduced in obtaining the wedge-constant. Through the use of monochromatic light, interference fringes, running parallel to the edge *D*, may be formed in the wedge-shaped air film between the two plates. By mounting the cryptometer on a dividing-engine and counting, under the microscope, the number of fringes lying in a known distance, the wedge-constant may be determined as accurately as we please—certainly better than a few tenths of 1 per cent.

SUMMARY.

1. A straight-line extrapolation of the brightness-hiding-power curve (from 70 per cent. brightness upwards) of a white paint, grayed with bone-black, passes through the point: 100 per cent. brightness, zero hiding-power. Comparisons of the hiding-powers of different paints and pigments at equal brightness may be carried out.

2. For the brightness range 75 per cent. to 83 per cent., the ratio of the percentage increase in hiding-power, to the percentage decrease in brightness = 5.0 for all white paints.

3. At "complete hiding" a gray paint film is much more transparent (less opaque) than a corresponding white film. Caution must be exercised in drawing conclusions relative to hiding-power from opacity measurements.

4. A modified cryptometer is described. The paint is prevented entirely from working under the areas of contact of the two plates.

This investigation was begun at the Experimental Station of the E. I. du Pont de Nemours Company, and was completed at the Johns Hopkins University.

Reverberation in Auditoriums. F. R. WATSON. (*Phys. Rev.*, Feb., 1923.)—The time it takes a sound in an auditorium to die away is approximately in proportion to the cube root of the volume of the room, while for the best effect the intensity of the sound generated should be in proportion to the square of the cube root of the same volume. G. F. S.

The Production of Artificial Vowel Sounds. SIR R. A. S. PAGET. (*Proc. Royal Soc.*, A719.)—In some manner we can usually understand what people say, whether they are children or adults, men or women, native or foreigners. We can recognize the same word though the sounds which we actually hear and translate into that word differ greatly according to the lips from which they issue. The author has been listening to the breathed vowel sounds of his own voice and has been analyzing them into two component notes of different pitches, due to resonance of the oral cavity. Sometimes these components are close together in pitch as in the "a" of calm and the "o" of not, or again they may be several octaves apart as is the case with the vowel sound of eat. The author has achieved considerable success in producing vowels with strangely shaped plasticine models to which artificial larynxes were attached, and he finds that good results come with two resonators placed either in series or in parallel. G. F. S.

ON UNIVERSAL AND OTHER CONSTANTS.*

BY

ENOCH KARRER.

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FROM a certain philosophic viewpoint the universe may be defined as a flux of things. On account of interactions giving rise to sensations, we feel that we may know something as to what or how the things do. As to what or how the things are we have no such immediate knowledge, but, by additional neural processes we make abstractions from our sensations and build up an analysis of what is this flux of things. It happens that, for most of us, most of the time a mere naming of the thing is a sufficient answer to the query: What is it? On close scrutiny we find that the thing named is, at any instant, a complex of stimuli that may give rise to a complex of sensations. It is this complex of sensations that we analyze from moment to moment to arrive at a knowledge of the thing in detail. The analysis leads to facts far removed from sensations, and onto paths quite inaccessible to sensations. Sensations are, after all, of a gross and practical nature. At the same time the conclusion which is arrived at in the practical world that the thing "exists" irrespective of the sensations is as inevitable as the sensations† themselves. For, although the abstractions leading to the concept and the naming of the thing seem to be the result of, or built up of sensations, we find that this process has already taken place when we become aware. It has indeed perhaps to a large extent taken place in

* Communicated by the Author.

† The analytic processes go so far as to lead to an inversion of the simple sequence narrated here. We formulate pictures of parts of the universe, and then, if they appear logically congruent, we strive to show that conditions can be found or defined under which our sensations or experience will be in accord with the pictures. The fact of the matter is that we have no hint as to what part consciousness or "self" plays in this interpretation of the flux of things. In all the physical sciences this is ignored, as I have done in presenting this viewpoint of the constants of nature. I cannot refrain from quoting one of my psychological colleagues who puts it thus: That the universe is such that it explains all of the constants, rather than that the constants explain the universe as the physicist would have it.

the animal nervous system, and merely awaits to be taken over into consciousness as exists in man.[1] Since it is by analysis that we know what the thing is, it may be said in a more or less paradoxical and misleading manner that things are what we think they are. Of course, it is all important what kind of thinking it is. Just in the same way, however, that in the sensations of sight, it is important what kind of seeing is done. A great practical difference is that the part of our nervous system that does the elemental seeing is more restrained and therefore less erratic than the part that does the thinking.

The fact then that we know things "to be," and the fact that we know about them through the sensations are coaxiomic.

There appears to be no limit to the extent of this analysis of the flux of things about us. The most essential elements of sensorial import that enter into it are the metrical aspects of time and of three dimensional space. It is a fundamental feature, too, that we find strata as it were, in the flux of things that flux differently relatively to each other. For we need to set surveyor's stakes or benchmarks into some stratum or other as reference points along the paths of our analysis. These benchmarks are the constants of science. Their constancy is only a relative matter. It suffices that it extend over sufficiently long intervals of time and space to allow us "breathing spells." As our experience and analysis proceeds we analyze the constants in terms of others that are more constant. There is probably no constant in the absolute sense that it is ordinarily looked upon in practice.

[1] We can find material suggestive of what I mean here in many cases of animal behavior, where a more or less complicated and coördinated series of reactions are involved. Take, for example, instances from among the wasps, the "mud daubers," which I have had many hours of pleasure in observing. Proper stimulus complexes lead them to form and carry mud pellets a great distance; and further stimulus complexes lead them to place the pellets systematically to form a housing, into which eggs are deposited in an orderly fashion, together with an ample supply of spiders well selected and preserved by inoculation to nourish the future larvæ. Errors may occur anywhere in these complicated performances, I have observed, for instance, that a wasp may carry mud for hours before it begins to deposit the pellets systematically in the same place. We have here certainly all the nervous substrata for such mental states that I am referring to. All that is required outside of perhaps more associational elements, is a cloak of consciousness or awareness, if it does not already exist.

Constants arrived at analytically and experimentally are the milestones of progress in our interpretation of the universe. It would seem therefore that, as data are piled up and theories are formed and reformed, a surveying glance over these constants properly classified, would give some assistance and pleasure. A simple classification is to call the constants independent [2] universal constants that apply to all matter, all electricity and to all processes, and from which all others may be derived; and to call others derived universal constants that are independent of materials and derivable from the first. A third class of constants are reference points by definition or experiment. A fourth class are the conversion factors [3] stating the relation between different units, and systems of units, and between different reference points. The fifth and largest class takes in the constants describing the properties of materials, and of instruments or mechanisms.

The purpose of the present note is chiefly to dwell upon a detailed classification of the independent universal constants, but I shall digress to give examples of the various groups in the following tables.[4] Those of the universal constants in groups 1 and 2 that are obtainable by independent measurement are marked with asterisks; those determinable with an accuracy sufficient to

[2] By independent is meant that the constants are not analytically functions of each other so far as is now known. How they may be related is shown by the constants derived from them. A better way of stating the fact is that all of the universal constants are interrelated in divers ways, but that a few of these relationships may be selected such that all others may be expressed in terms of them. The decision then as to which constants are independent rests upon one's viewpoint. See also footnote 11 below.

[3] For the most part conversion factors other than unity are like erasures or, rather, like corrected connections between lines drawn from two directions that do not meet as intended, on the scroll upon which our picture of the universe is being depicted.

[4] The constants which I give here are selected from a list and classification of constants that were reported to the National Research Council through Dr. E. P. Hyde, Director of Research, by a committee consisting of Drs. E. Q. Adams, W. E. Forsythe, A. G. Worthing and E. Karrer. I am departing somewhat from that classification both in the designation and in the number of groups. The constants given in group 1, however, are taken in their entirety from the committee report. Although the present stimulus for this communication has largely been the committee work, yet I have entertained the idea for sometime of making some such contribution with the object of showing the proper place for certain concepts that have recently entered into the literature of photometry and illuminating engineering.

warrant their use in calculating others, including those with single asterisk, are indicated with double asterisk.

All numerical values are based upon the fundamental units: Centimetre, gram, second, degree (K.), $^1/_{16}$ of the atomic weight of oxygen, and the dielectric constant of free space; and, being illustrative merely, are given for the most part to two significant figures only.[5]

1. Independent Universal Constants.

Symbol.	Numerical value.	Name.
c	$^{**}3.0 \times 10^{10}$ cm. sec.$^{-1}$	Velocity of light in free space.
γ	$^{**}6.66 \times 10^{-8}$ g.$^{-1}$cm.$^{+3}$sec.$^{-2}$	Newtonian gravitational constant.
e	$^{**}4.8 \times 10^{-10}$ c. g. s., e. s. u.	Electronic charge.
m_o	9.0×10^{-28} g.	Mass of isolated resting electron.
m_p	1.6×10^{-24} g.	Mass of proton (in heavy elements).
k	1.4×10^{-16} erg. p. °K.	Molecular gas constant, coefficient of Boltzman's entropy equation.
h	6.5×10^{-27} erg. sec.	Planck's constant, quantum of action.

2. Derived[6] Universal Constants.

Symbol.	Formula.	Numerical value.	Name.
	e/m_o	$^{**}5.4 \times 10^{17}$ e.s.u.g.$^{-1}$	Bucherer constant.
	$e/m_o c$	$^{**}1.8 \times 10^{7}$ e.m.u.g.$^{-1}$	Bucherer constant.
	ch/e	$^{**}4.2 \times 10^{-7}$ erg. cm. e.s.u.$^{-1}$	Photoelectric quantum.
	k/e	$^{*}2.9 \times 10^{-7}$ erg. per e.s.u. °K.	Thermoelectric quantum.
e_a	$2e_3$	$^{*}9.5 \times 10^{-10}$ c.g.s.e.s.u.	Charge on α-particle.
N_∞	$\frac{2\pi m_o e^4}{k^3 c h^3}$	$^{*}1.1 \times 10^{5}$ cm.$^{-1}$	Rydberg wave number (according to Bohr).
c_2	ch/k	$^{**}1.430$ cm. °K.	Second constant of Planck's radiation law.
σ	$\frac{2\pi^5 k^4}{15^2 h^3}$	$^{*}5.7 \times 10^{-5}$ erg. cm.$^{-2}$ sec.$^{-1}$ °K.$^{-4}$	Stefan-Boltzman constant.
F	$10\ Ne/c$	$^{**}9.6 \times 10^{4}$ coulombs per mol.	Faraday's constant of electrolysis.
F_p	F/m_p	2.58×10^{4} coulombs per mol. g.$^{-1}$	Ditto for gram of hydrogen.
R	$Nk/10^7$	$^{**}8.3$ joules per mol. °K. / 2.0 cal. per mol. °K.	Molar gas constant.
$\lambda_m T$	$c_2/4.9651$	$^{*}0.29$ cm. °K.	Constant Wien's displacement law.
N	$1/m_p$	$^{*}6.1 \times 10^{23}$ g.	Number of molecules per gram molecule.
n		2.7×10^{19} cm.$^{-3}$	Loschmidt's number. Number of molecules in 1 c.c. NPT.
	$1/\mu$	$^{*}9.0 \times 10^{20}$ cm.^{3} sec.$^{-2}$	Kinematic elasticity of ether.
c_1	$2\pi c^2 h$	3.7×10^{-5} erg. cm.^{2} sec.$^{-1}$	First constant of Planck's radiation law.

[5] The two underscored constants are among those referred to in the previous footnote.

[6] How they are derived from the independent universal constants is indicated in the second column where the formulas are given.

Symbol.	Formula.	Numerical value.	Name.
ν_∞	$cN\alpha$	3.3×10^{15} sec.$^{-1}$	Rydberg's fundamental frequency.
α	$2\pi e^2/hc$	5.30×10^{-10} sec.$^{-1}$	Bohr's constant for fine structure of spectral lines.
a_1	$2e^2/3m_oc^2$	1.9×10^{-13} cm.	Radius of Lorentz surface-charged electron at rest.
a_2	$4e^2/5m_oc^2$	2.2×10^{-13} cm.	Radius of Lorentz volume-charged electron at rest.
ϵ	$^3/_2k$	2.1×10^{-16} erg. per °K.	Temperature coefficient of energy of monatomic gas molecule.
a	$4\sigma/c$	7.6×10^{-15} erg. cm.$^{-3}$ °K.$^{-4}$	Coefficient of Stefan-Boltzman law for density of radiant energy.
m_H	$1.008 \times m_p$	1.7×10^{-24}g	Mass of resting neutral hydrogen atom.
m_{He}	$3.99 \times m_p$	6.6×10^{-24}g	Mass of resting neutral helium atom.

3. Reference Points.

(By definition and experiment.)

Symbol.	Numerical value.	Name or definition.
g	980 cm. sec.$^{-2}$	Acceleration of gravity at sea level and 45° latitude.
T_o	273.13 °K.	Freezing point of water (absolute centigrade scale).
V_o	22.4 litres in mol.	Volume of gram molecule at NPT (normal pressure and temperature).
c_v	$3R = 6.0$ cal. per mol. °K.	Atomic heat of solids (Dulong and Petit).
d_c	3.0×10^{-9} cm.	Grating space of calcite.
λ_{cd}	6438.47×10^{-8} cm.	Wave-length cadium red line in terms of which the meter has been measured

and many others, such as the magnetic permeability, the density and viscosity of air, etc.

4. Conversion Factors.

Symbol.	Numerical value.	Name or definition.
J	4.2 joules per cal.	Ratio of joule to the mean calorie, thermo-mechanical conversion factor, mechanical equivalent of heat.
$1/P_m$	0.00150 watts per lumen	Minimum ratio of watt to lumen ($\lambda - 556m\mu$), photo-mechanical conversion factor, mechanical equivalent of light.[7]
P_m	667 lumens per watt	Maximum ratio of lumen to watt, visibility[8] of light at $\lambda = 556m\mu$.

[7] This last phrase has misleading historical connotation, and either of the first two are preferable to it. It gives to the factor the significance that the mechanical equivalent of heat once possessed but no longer retains. (See Buckingham, *Phil. Mag.*, p. 710, 1921.)

[8] The nomenclature should be so adjusted in any one department of science that all duplicity of meanings is avoided. This is not true with the word visibility in optics. In addition to the above use there is the visibility of objects and of interference fringes. For the latter case we have the well-known visibility curves. (See note 9.)

5. Constants of Materials and of Instruments.

A. Constants of Instruments Used in
1. Physics.
a. Mechanics.
Statics.
Dynamics.
Sound and acoustics.
Heat and thermodynamics.
b. Electromagnetics.
Electrostatics.
Electrodynamics.
Radiation.[9]
Photic[10] radiation.
1.5×10^{-9} ergs. $sec.^{-1}$ theshold of dark adapted eye.
0.006 Weber's constant at ordinary brightness.
Ultra-photic radiation.
Gamma rays.
Röntgen rays.
Ultra-violet.
Infra-photic radiation.
Infra-red.
"Rest strahlen."
Hertz radiation.
Wireless waves, and longer.
} Extra-photic radiation.
2. Physical chemistry.
3. Chemistry.
4. Engineering.
5. Biology.
etc.
B. Constants of Materials.
Subdivisions and subheads as suggested in A.

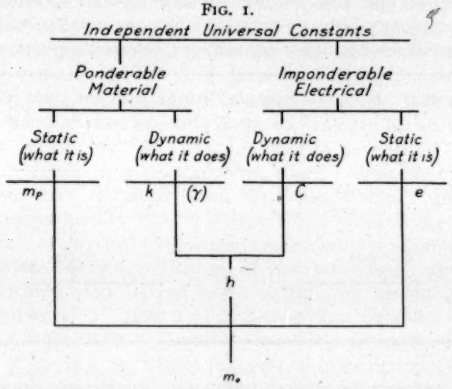
Returning to the independent universal constants, it is seen that seven of them may be selected such that all others may be expressed in terms of them. The seven given in group 1 appear to be the simplest analytically. It is interesting that the number is small—seven in the present state of knowledge and possibly

[9] To avoid entirely the objections noted in footnote 8, the word photic is used instead of visible. The Latin prefixes are preferred to the Greek prefixes (hyper and hypo), because one of the latter is already attached in the word hypo-phonic (musical term) to a meaning different from that desired here. The Latin prefixes allow terminology in acoustics similar to that suggested here for optics. From one viewpoint optics and acoustics are subdivision of radiation.

[10] The examples given here would of course fall under proper subheads. They are inserted to show that the sense organs may be treated as instruments in so far as they have constants that are of practical importance to any particular science, such as the eye has in photometry.

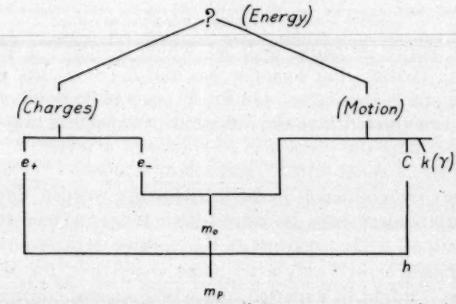
only six, as will be indicated later.[11] These seven may be further superficially classified according as to whether they pertain to ponderable matter or to electricity. The constants m_p, γ and k

FIG. 1.



A chart suggesting a classification of and the relationships between the seven independent constants, based upon the notions *ponderability* and *imponderability*.

FIG. 2.

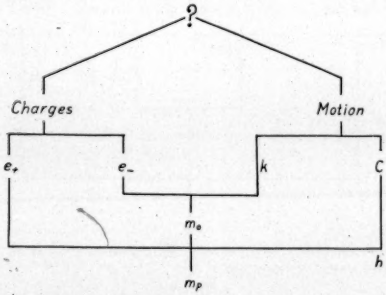


A chart suggesting relationships between the seven independent constants, under the two notions of *charges* and *motion*. For the symmetry of this chart see Fig. 3.

[11] The number of fundamental units of measure is less than seven, so that on further analysis there must appear a lesser number of independent universal constants. Since the writing of this paper there has come to my attention an interesting paper by Lunn (*Phys. Rev.*, July, 1922) who gives considerations bearing upon this point.

distinctly are those pertaining to gross ponderable matter, while e and c are those belonging clearly to the electrical. There are left then m_0 and h which are not so easily disposed of in this classification, but hold rather an intermediate position; since m_0 is a property of the electron (e) but has ponderability, and h is a factor somewhat like c pertaining to electromagnetic radiation but in fact is always associated with an m_p. It may be noted, however, that this classification brings out the fact that these

FIG. 3.



A symmetrical chart suggesting the relationships between the seven independent constants classified under the two categories, *charges* and *motion*.

constants occur in pairs, each of which contains a static and a dynamic factor. For example, m_p and k (or γ) are a pair, as are also e and c, leaving m_0 and h. From a philosophic viewpoint it might be expected that the independent constants may occur in pairs, describing the properties of things in a way to answer the two queries: "What is it?" and "how it does?" This duality has already been hinted at in the introductory words. Our answer to the latter query may be traced back more or less directly to the sensations. The answer to the former is arrived at, even in its simplest aspect, only after some analysis of the sensations. Similarly, it might be expected that where several constants occur in reply to either query, only one would stand out as preëminent, and the others as derivable from or as incidental to it. This may be the case with γ or k, and since most attempts at theories of gravitation strive to give γ in terms of other constants, I have subordinated γ rather than k. The essence of the whole philosophy

of the conservation of energy, in so far as it has had historical significance in heat, is embodied in k. The classification of the independent constants has then a duality at all points. In Fig. 1 given below to represent these ideas, h and m_0 are put in an intermediary place as might be done if they are thought of as the pair of constants resulting from the interaction of ponderable matter and electricity. The diagram in Fig. 1 is not satisfactory. It is not well balanced in many respects. This classification is one that may be made if the equivalence between electromagnetic inertia and gravitational inertia is entirely ignored. The latest trends in physics do not allow a division of subject matter into the "electrical" and the "ponderable." In another attempt represented in Fig. 2, I have borne in mind that present-day analysis of physical phenomena emphasizes two things, motion and electrical charges. Further, if one considers c the motion constant where velocities of great or limiting magnitude enter, and k as typical of motion constants where velocities of small magnitude enter, then k might appropriately be inserted to antecede m_0 as in Fig. 3, which becomes a more symmetrical one. Our ordinary concepts of matter and electricity are associated with the central and left portions respectively, while those of radiation are associated with the extreme right portion of the chart.

A New Industrial Factor, the Utilization of the Calories Furnished by Hot Springs. J. DYBOWSKI. (*Comptes Rendus*, March 12, 1923.)—Since the destruction of the mines of coal in and about Lens by the Germans, France has been seeking to find means of utilizing to the full any sources of energy she may have. Winds, tides and rivers have been laid under contribution to replace in some measure the loss of coal due to the invaders. Now it is the turn of the hot springs to be harnessed in the service of man. The low temperature of the waters imposes very evident limits on the use to which they may be applied. They readily lend themselves to domestic uses or to bathing installations. In the distinctly industrial field is the heating of hothouses for the raising of early vegetables. Such an experiment has been made in the southwestern part of France in the department of Landes at Prechacq.

Let there be a spring yielding 50 cubic metres per hour of water at 62° C. If this after utilization is discharged at 25° C. it will liberate in an hour 1,850,000 large calories. The author reckons this to be equivalent to the burning of 1057 kg. of coal per hour, or of about 25 tons per day. The waste of heat from the water should not exceed 10 per cent. in a well-organized plant.

Not all hot springs can be thus utilized. If the water be below 60° C., or if it be too strongly impregnated with minerals or gases, it can not be used to advantage. Of course the climate in the region of the spring makes much difference. A low temperature will cause great loss of heat. Besides this the place where the hothouses are can not be too far from the spring owing to losses in transmission. In the plant at Prechacq the water issues from borings at a temperature of 63° and is led 2.3 km. (1.8 miles) to a series of greenhouses, each covering a quarter of a hectare (half an acre). The total area warmed is 10 hectares, 23 acres. G. F. S.

Velocity of Sound in Sea Water. E. B. STEPHENSON. (*Phys. Rev.*, Feb., 1923.)—It is illuminating to compare the experimental methods here used with those employed by Colladon and Sturm in their classical determination of the velocity of sound in lake water in 1827. The experiments here described were conducted in Block Island Sound in January, 1922. The method "consisted in electrically detonating a .5 kg. bomb of TNT at a depth of 8 to 10 metres, and simultaneously sending a radio signal at a distance of approximately 18,000 metres from shore. The sound through water was received by a series of five hydrophones . . . connected by cable to a central shore station. . . . A string galvanometer with six strings, a tuning fork controlled timing device, and a photographic recording camera, gave a record of the vibrations of the strings with transverse timing lines at .01-second intervals." It was possible to read the intervals between the instant of explosion and the time of the arrival of the sound wave at the hydrophone to .001 second.

The location of the hydrophones was determined at the time they were placed in position by observations from the shore. "The location of the bomb at the instant of firing was determined by observations on the target (attached to it) from three shore stations on two base lines about 10,000 metres each in length." The chief difficulty in the work lay in finding a time when all the factors were in favorable conjunction. "This was particularly true of the visibility, since it was necessary to observe the target simultaneously from three observation stations at distances of approximately 16 kilometres, and to read its angular position to .01°."

The final average of the velocity is 1453.3 metres per second. The temperature of the water was −.3° C. and its salinity 3.35 per cent. G. F. S.

Sound Transmission of Sawdust Concrete. D. L. RICH and C. R. BROWN. (*Phys. Rev.*, Feb., 1923.)—Slabs of concrete containing sawdust were cast with the thought that the resulting material would be light in weight and would in addition be a poor conductor of sound on account of its porosity. Strange to relate, the slabs with a high sawdust content proved to transmit sound better than solid concrete itself. G. F. S.

THE SENSE OF VERTICALITY AND ITS APPLICATION TO LIGHTHOUSE WORK.*

BY

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WHEREVER navigators have to lead boats through difficult waters, means to show the navigable channel have to be provided for. During the day, natural marks in the landscape have been for centuries, and are still, to a great extent, the only guides used by mariners acquainted with the locality. In much frequented waters, however, and at night, more reliable aids had to be installed. Floating bodies, moored at the proper place, are the usual means of marking a channel when the latter is at all crooked or exceedingly narrow; the design of buoys has been wonderfully improved in the last thirty years and to-day light buoys, bell buoys, whistling buoys, buoys with submarine signal attachment and others are used all over the world. But this method of marking navigable waters is expensive and when the channel is straight over a reasonable distance and is free from obstacles, it has been found cheaper, and most often more convenient, to mark its axis by means of two stations, generally high towers provided with powerful lights and placed at one end.

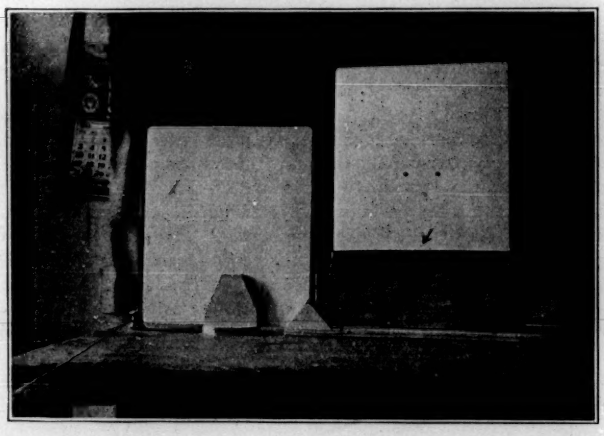
Boats follow the channel as long as they keep in line with the two marks. In practice, however, the mariners cannot use these marks as a surveyor would two rods to run a straight line; the latter conceals the farther rod with the nearer one and, from time to time, ascertains that he has both still in line by stepping on either side and thus "opening" the rods; the mariner, having no such freedom of motion, must at all times see both lights. To secure this result the back tower is considerably higher than the front one, their respective heights being calculated so that from the farthest point of visibility the two lights appear still as distinct, *i.e.*, subtend an angle of not less than four minutes according to the most generally accepted rule. Then, of course, the problem facing the mariner is no more that of placing two rods in line

* Communicated by the Author.

with his eye, but to put two points on a same vertical; and to what extent our "sense of verticality" can be relied upon is still an open question.

In 1864, Léonce Reynaud, in his "Mémoire sur l'Eclairage et le Balisage des Côtes de France," suggested as a limit for the possible error the quarter of the angular distance of both lights increased by four minutes. This rule errs obviously on the safe side and would necessitate very expensive ranges, the more

FIG. 1.



so since L. Reynaud recommended at the same time a minimum angular distance of from eight to fifteen minutes, according to the power of the lights.

In 1902 (*Ann. P. Ch.*), M. de Joly made a new study of the question and found the error in the estimation of verticality "nearly negligible." This, however, does not offer any safe rule for the calculation of the distance between the two lights of a range, and the usual practice among lighthouse engineers has been to take as the minimum of the distance of the two lights a set fraction of the useful length of the range—generally from one-tenth to one-twelfth.

This method is obviously unsatisfactory since it would lead to give the same sensitivity to two ranges used to mark, say, one a channel 400 feet wide, and the other, a pass half a mile large, if in both cases the point of maximum danger happened to be located at the same distance from the front light. Safe and reasonable results cannot be obtained unless the angular distance measuring the "opening" of the two lights at the edge of the channel is introduced in the calculation. This angular distance should be such that the non-verticality of the line passing through the two lights could then not be questioned.

In order to ascertain what could be considered a safe limit beyond which the two lights should appear on two different verticals, the writer has endeavored to realize in the laboratory conditions somewhat similar to those of a range, and has measured the angular distance between the verticals passing through two very small lighted and movable points which observers had been requested to place on the same vertical line.

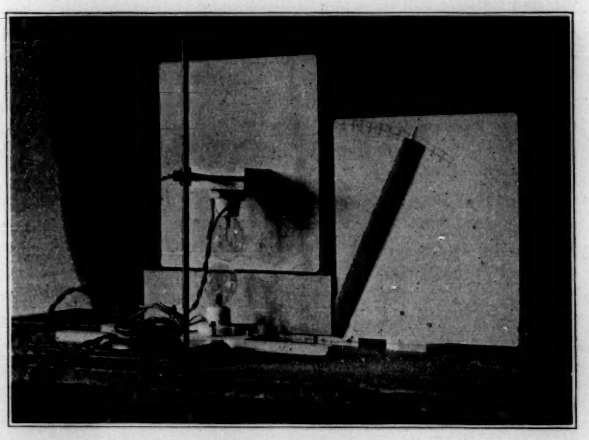
The Apparatus.—The apparatus consisted essentially of two electric lamps in front of which were placed screens with pin-holes, one each. The upper lamp was fixed, while the lower was mounted together with the screen on a carriage sliding between two parallel strips of wood and placed so that the two screens would be in the same plane. An endless string was fixed on the carriage, passed on idlers fixed to the table which carried the whole apparatus, and was attached to a drum placed in front of the observer; by this means, the later, who was some thirty feet distant from the screens, could move the lower one to bring it to the position which, in his judgment, placed the two lighted pin-holes on the same vertical. The left end on the movable screen was abutting against a lever fitted with a needle which moved on a fixed dial, the latter having been empirically graduated to read small displacements (1/50 of an inch), and an assistant to the observer, placed on the light's side of the screens, read the position each time the observer declared himself satisfied that he had both pin-holes "in line."

The distance of the pin-holes was varied and, of course, it was found that the difficulty of correctly placing the lights increased after the angular distance passed a certain limit. Later the experiment was repeated with a sector of paper on which a black line had been drawn; when the line was heavy enough to be

very readily seen, it seemed that the observer experienced much less difficulty in determining the vertical than he did with the first arrangement; the line, however, had to be comparatively long and subtended an angle of 2°.

Results.—The most comprehensive series of tests was made with the pin-holes at an angular distance of 0°22′ which corresponds for two range lights seen at a distance of two miles to a difference of level of some 75 feet, a difference of height very

FIG. 2.



rarely reached. The conditions in the rooms where the experiment was carried out made it advisable not to try a lesser angular distance and since other observations showed that the sensitiveness of the readings decreased when the angular distance of the lights increased, one would seem justified in considering the results obtained as erring on the safe side.

In this series of tests, eleven observers, of very mixed training and ability, were requested to take readings, six for each observer. The results are given in Table I.

Five of the observers were obviously quite better than the others. Taking the average and the maxima in each case, we obtain the following results:

Average of 11 observers $\left\{\begin{matrix} -26'' \\ 40'' \end{matrix}\right.$

Average of 5 best observers $\left\{\begin{matrix} -20'' \\ 20'' \end{matrix}\right.$

Maximum of 11 observers $\left\{\begin{matrix} -1'\,14'' \\ 1'\,46'' \end{matrix}\right.$

Maximum of 5 best observers $\left\{\begin{matrix} -46'' \\ 56'' \end{matrix}\right.$

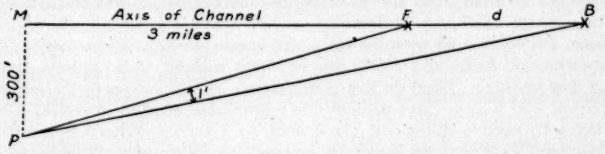
TABLE I.

Observers / Readings	A	B	C	D	E	F	G	H	I	K	L
1	−18″	4″	−18″	32″	1′14″	1′46″	− 12″	22″	1′38″	44″	1′6″
2	− 8″	56″	−32″	− 4″	1′ 0″	50″	−1′ 6″	−32″	32″	8″	56″
3	−22″	4″	−22″	−10″	− 6″	1′ 6″	8″	18″	56″	−36″	22″
4	30″	26″	− 4″	30″	0	1′24″	− 36″	−26″	56″	−10″	− 12″
5	22″	4″	−18″	−46″	46″	50″	−1′14″	− 4″	1′20″	−46″	22″
6	0	12″	−46″	− 8″	40″	50″	− 46″	−30″	1′ 6″	−56″	6″
The five best	*	*	*	*	*						

In all the above the error of verticality is expressed by the angular distance betwe the actual position of the lower light and the one it should occupy.

As was to be expected, though the angular distance between the position of the lower light and that of the vertical passing

FIG. 3.



through the upper light increases when the angular distance of the two lights increases, the angle between the line joining the lights and the vertical decreases. Thus while this angle for the average error of the present series of tests was 2°, it was found to be half of that amount when the two lights subtended an angle of 1°30′.

Conclusion.—From the foregoing it would seem that an eye, trained as is that of the average mariner, should be able to detect readily for two lights a lack of verticality of less than 1′, the angle being the angular distance between one of the lights and its proper position with respect to the other. In other words, the horizontal angle subtended by the verticals passing through the two lights seen from the edge of the safe channel should not be less than 1′. Thus to mark a channel of 600 feet by a range, the front light of which would be located three miles up the channel, the minimum distance of the back light should be calculated as follows:

$$MP \tan \widehat{MPB} = MF + FB \quad \text{with} \quad \widehat{FPM} = \text{verstan} \frac{MF}{MP}$$

$$\text{or} \quad FPM = \text{verstan} \ 60.8 = 89° \ 3' \ 28''$$

$$\widehat{MPB} = 89° \ 4' \ 28''$$

$$300 \times 61.90 - 18{,}240 = d = \text{say } 330 \text{ feet}$$

Distances thus obtained may still be somewhat empirical; they are, however, a nearer approximation to truth than those based on the old rule of a set fraction of the distance or similar ones, since they introduce in a rational way the main factor of the problem, *viz.*, the width of the channel at the distance where the danger is maximum.

Electrical Properties of a Flint Glass of Density 6.01. G. L. ADDENBROOKE. (*Phil. Mag.*, March, 1923.)—The approximate composition of this glass is SiO, 22 per cent.; PbO, 78 per cent. "Judging by its density and composition, the density of natural silica being 2.61, fused silica 2.0, and lead 19.2 (?), it must contain over 30 per cent. by volume of metallic lead. It breaks easily, though hard. It softens and melts at a fairly low red-heat without showing any signs of blackening. That such a composition should be perfectly transparent and a high-class insulator is remarkable enough in itself." It has a refractive index for the D-line of 1.9201. When one forms Maxwell's ratio of the dielectric constant to the square of the refractive index the quotient comes out equal to 3.55. Other specimens of flint glass of different densities give for this ratio a series of values increasing as the density increases. For the flint glass of density 6.01 the dielectric constant is 13. "So far as I am aware this is not only the highest dielectric constant yet found for any glass, but it is the highest found for any material not of abnormal character and not complicated by the effects of absorption." G. F. S.

MEASUREMENT OF THE WORK IN CRUSHING.*

BY

ERNEST A. HERSAM.

Associate Professor of Metallury, University of California.

THERE is a problem that has been handed down through the years, which remains a drag upon the milling industry of the present day. It is the problem of establishing the basis for measuring the work accomplished in crushing. Milling requires its solution, and needs assurance of the correctness of its grounds. Opinion, unsupported, is never to be accepted in the place of proven fact, and though the opinion of the industry has been fairly uniform, there has not been perfect agreement, owing to the want of expected mechanical demonstration with absolute precision. All mechanical demonstration is accompanied by interferences and limitations that obscure the real law. Though mechanical demonstrations of every detail of this operation are so abundant as to make the assembling of these details a matter of the merest common-sense, the lack of precision in the entire connected operation fails to satisfy those who would demand the last extreme in the offering of proof. In judgment here, as in every scientific judgment, from that of the conservation of energy to the theory that the earth is round, mechanical attainment requires the supplement of constructive reason to reveal the truth available in proven fact. Just as it would seem grievous to stay the progress of milling to demonstrate the law of gravitation, so it is wasteful to occupy a modern day with the discussion of this problem, if we may discover that we are agreed.

The evidence which appears awaiting to be recognized, and which is in common possession, is to the effect that the work of crushing is shown by a surface relation, and, other things being equal, is proportionate to the total of new surface produced by the operation. So long as any cloud rests upon the tentative truth of this assertion there will be impediment to advancement in milling practice, where power-consumption and utilization are important. Already the indecision has cost the industry too much.

* Communicated by the Author.

The attention of everyone who does not concur in these opinions is called to this matter. The desire is not to prolong the discussion, but to learn if the practice is not now able, with security, to end it, by reasons which appear to be irrefutable and final.

The point at issue is the interpretation of size-measurement in terms of work. People do not feel quite satisfied or convinced. The discussion flares up at times, as though it were a lingering flame on a field where once the fire of contention had been. But there has been no real contention. The recurrences are due, in most cases, to unmindfulness of published fact; but they leave the feeling of doubt in the general mind. If the reader is in agreement with the statement that the accomplishment in crushing is represented by the total of surface produced, he may proceed in the expectation of scientific progress and improvement. If, on the other hand, he believes otherwise, and has become entangled in the so-called "Kick's Law," there is need for him to go carefully into the matter, and, if necessary, to review the literature that throws light upon it.[1] The pity is that there is so little of

[1] Literature having direct bearing upon this subject is as follows:

"Lehrbuch der Aufbereitungskunde," P. Ritter von Rittinger, p. 20 *et seq.*, Berlin, 1867.

"Das Gesetz der Proportionalen Widerstände und Seine Anwendungen," Friedrich Kick, 1885, Leipzig, p. 1 *et seq.*

"Ore Dressing," R. H. Richards, 3, p. 1325 *et seq.*

"Economy of Power in Crushing Ore," E. A. Hersam, *Mining and Scientific Press*, 1907, **95**, No. 20, p. 621.

"Grading Analyses and Their Application," H. Stadler, *Trans. Inst. of Min. and Met.*, 1909–10, **19**, p. 478.

"Mechanical Efficiency in Crushing," Algernon Del Mar, *E. and M. Jr.*, 1912, **95**, No. 24, p. 1129.

"The Crushing-Surface Diagram," A. O. Gates, *E. and M. Jr.*, 1913, **95**, No. 21, p. 1039.

"The Work of Crushing," Arthur F. Taggart, *T. A. I. M. E.*, 1915, **48**, p. 153.

"An Investigation on Rock Crushing Made at McGill University," John W. Bell, *Trans. Canadian Mining Institute*, 1916, **19**, p. 151.

"Kick *vs.* Rittinger: An Experimental Investigation in Rock Crushing, Performed at Purdue University," A. O. Gates, *T. A. I. M. E.*, 1916, **52**, p. 875.

"Kick *vs.* Rittinger: An Investigation of the Laws Governing Crushing in Ball Mills," E. A. Rolph, *Canadian Min. Jr.*, Aug. 18, 1922, p. 550.

substance to have occasioned the continuance of the discussion. When we shall have taken the brief time necessary to consider the matter, it is possible that we shall be agreed, and that the "Law of Kick," as offered to us, can be allowed to drop.

In order to know the efficiency of a crushing operation, we have to know, of course, the power applied and the power utilized. The quotient is the efficiency. In every judgment of efficiency, the consideration is limited to a definite case. The purpose is to determine something set apart, as a kind of rock, a kind of machine, a way of crushing. Whatever the quantities are that are used, or the manner in which the work is done, or the kind of appliance, the conditions have to be known. These can be described. They are uniform in all similar cases, and being held constant, may be eliminated from consideration without the requirement of a numerical assignment of values to them. They are the constant conditions. The choice of units does not matter.

There are, however, two considerations that are fundamental, which cannot be explained away by the manner of doing the work, nor by the hardness of the rock, nor the crudeness of the appliance. They are the real and fundamental variables that enter the calculation of efficiency. The one relates to the useful effect, and measures it, the other refers to the valuable power, and records it. It is suitable to call the first *accomplishment*, and the second *expenditure*.

Efficiency does not enter the consideration of accomplishment until some standard of accomplishment is known in terms of expenditure. Having this, it is possible to see efficiency as a ratio between the accomplishment in the specific case and that of absolute practice. Efficiency then, being a ratio, may be expressed in percentage, upon multiplying the ratio by one hundred. The units that enter it are combined units of accomplishment and expenditure. Such units are: The degree of fineness of the product, the horsepower, or, in fact, units of any other chosen kind capable of conversion. Being in ratio, they do not affect the results by their nature, but rather only by their relative magnitude, but in representation they must be truly expressive of actual expenditure and of real accomplishment.

In this ratio, we find no escape from the requirement of a numerical expression to show the accomplishment as well as the expenditure. Unless we know what the accomplishment is, and

can agree upon it, we cannot discuss efficiency, nor can we make any real scientific progress in matters that relate to efficiency. Having this numerical expression, we can take the highest value, or ratio, that was ever known, as obtained from the best work that was ever done, to be the temporary standard of efficiency. Such a standard held before us as ideal suffices while there is no other basis, and gives us the beginning of scientific comparison; but without the measurement of accomplishment, we are deprived of even this. It is clear that it is necessary to obtain, in numerical form, the expression of accomplishment in crushing, or of the degrees of accomplishment.

Rock that has been through a crusher, unquestionably, is changed in appearance. It is changed, possibly, in many ways that we do not see. It may be hot from friction, or bent by deformation, or under strain. The purpose that we had was to crush it. The effect that we got was this accomplishment and something more; but the accomplishment that we would measure is the crushing done, and nothing else. While it is easy to see, upon examining the rock, that something happened, difficulty arises when we undertake to judge the desired result, to exclude from it the useless things that happened, and to assign to it work-units. We must find the inherent quality that represents the desired effect, and measure it. We must examine the differences so closely as to be able to state the extent of the benefit. There is required then something which may guide us in excluding from the unit of accomplishment all the varying, opposing influences, and to rate such influences not as profit but as loss.

In judging the crushing of rock we encounter great complexity that comes from the comparison of dissimilar things. The one purpose is to make the rock fine. The measurement of work done is, therefore, a measurement of fineness. If anything other than producing fineness was done, it was done to no purpose. All else is outside the consideration, and is likened to resistance or to waste. The measurement of what was done is the measurement of the fineness. We are compelled to state what fineness means, and to express the degree of it. It must represent the total of accomplishment, based upon the total reduction in the size of all the components of the material as represented in all of the variously sized constituents of the product.

It is necessary, now, to see that our perception of the size

of anything relates to various dimensional attributes, of which the volume is only one. We are justified in representing size in any of these aspects, according to the manner in which the object functions, but in every case must affix the conditions, and affirm the degree. The size of a solid object, under conditions of similarity of shape, therefore, is truly represented by a dimension, by the surface, or by the cubical content. Each aspect is a consideration apart. Each may be represented by another upon affixing the corresponding index, but when converted, the conditions are distinct. The simple requirement here, for reasons that we shall see, is to represent the size of particles in terms of the surface of such particles.

The surface significance of size is necessary, in crushing or grinding, because of the fact that the rupture of solid substance, while it changes both the volume and dimension of the separate pieces, arrives at this result by severing the cohering molecules that lie along a plane. New exposure, or new surface is made by driving the flaw, fracture, or cleft, into an interior, and applying such energy as to produce this new surface in opposition to the force of solid cohesion. Molecular disturbance varying with the hardness and other qualities of the rock necessarily occurs beneath the surface, for the surface is but the ideal of area without substance. But the disturbance, which is represented by the alteration of the surface, is an exchange of energy in the adjustment of molecular forces that are affected by the surface to meet the requirements of surface structure. Being thus of the constant depth, required by nature of the substance, the surface alteration, so far as this may include the idea of volume, is proportionate to the surface. Such work, whether of deformation or of rupture, is dependent upon the hardness of the rock, and per unit of surface is a constant for each kind of rock under conditions of maximum efficiency.

It is necessary to see, at the beginning of the consideration, that the total of all the new surface of all pieces contained in a definite quantity of crushed rock of given hardness represents the accomplishment of crushing, whatever energy was required to do the work. The mass is conceived as being broken out from a solid mass of rock, and broken down to the condition in which we have it. Such rating may be made conveniently by employing Gates' reciprocal. In any case, we must see that the work is

proportioned to the surface, and is not dependent upon a third linear unit that is distributed indefinitely within the volume of the uncrushed pieces.

Mr. H. Stadler,[2] under the opinion that he had discovered important contradictions to prevailing beliefs, introduced a third dimension, representing the dimension of the pieces. The third dimension would make the work accomplished in crushing each particle dependent, not upon the surface, but upon the volume, and correspondingly would alter the basis of representation of the work expended upon a given mass or accumulation of these pieces. The idea arose from the fact that there is a force normal to the unbroken surface, functioning as deformation, against which all rupture must be performed, through a distance influenced by the diameter of the particle. Modifying the surface by the new factor changes surface into solid, raises the equation to the third degree, and suggests volumetric expression of accomplishment for the total of the solid particles.

We must see, however, that many factors could be introduced that would add to the conception of the occurrences of crushing and seem to depart from surface representation. But like this one, they are not constant and are not a necessary part. Even if the effects coincided to a large extent with this supposed dimension, they would only the more deeply involve us in a misconception and the more effectually conceal the need of a true interpretation to show the nature of the work. Mr. Stadler fails to bring out the time factor that conditions the depth of plastic deformation, and fails to observe the real difference between the elastic and the plastic factors. He would have to tell us that, by his reasoning, the work done in sawing a plank into two shorter planks is conditioned not upon the cross-section, made by the given saw, but depends upon the length of the plank. Similarly, by such reasoning, knowing of the existence of elastic strain, and knowing that it is present not only within the rock but beneath all acting surfaces, he would have to rate as useful, the work done upon the metal liners, conditioned not by the size of the ore, but by the size of the machine. He refers to the work of Friedrich Kick as confirming his own conclusions in a statement that he singles out as "Kick's Law," drawing conclu-

[2] *Ibid.*

sions, which we are compelled to observe that practice does not support.

The component that deformation actually introduces is a vague quantity that varies, sometimes, somewhat according to the dimension, but is dependent upon the manner in which the operation is performed. The deformation that is elastic, is available, and may be given back again in doing work; and, in efficient operation, should be recoverable in appreciable proportion. The deformation that is plastic is permanent deformation. It is accomplished with internal friction. The energy that produces it practically takes the form of heat. It is variable, depending upon many conditions, such as prevailing temperature and velocity; but so far as it occurs, it should be measurable as heat. No person can desire to include this waste heat as a component of the useful work of crushing. Everyone can see that it is possible to produce much heat with no appreciable crushing. For example, one may hammer a small mass of malleable lead until it is hot without the beginning of a rupture. Similarly, it is possible to do much crushing with little heat, increasing velocity and shortening the time until deformation becomes much diminished. The heat should attract our attention as one of the losses, along with vibration or with the noise that is made. It doubtless should be measured, but to put heat and deformation into the accomplishment of crushing would pervert all ideas of efficiency, and hopelessly conceal real differences under a changeable and false standard.

It is, in a measure, objectionable, and may be found to be unfair, to compare the results obtained in coarse crushing with other results, perhaps corresponding, obtained in fine crushing. Hard grains, which escape fracture in the coarse crushing, consume great power in fine grinding. Cleavage, jointing, and minute fissuring, introduce lines of weakness that often develop at some definite size. In all these cases we are dealing with a rock having qualified hardness. The qualification of hardness, solely as to direction, becomes eliminated in the average hardness of the rock in all directions. The hardness qualified as to size, through nodulization, crystallization or other prevailing structural peculiarities, are qualities which crushing-tests, in many cases, are designed to show. None of these qualifications impose permanent complications upon interpretation. Computations are

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based upon homogeneous rock. Departure from homogeneity is recognized and given such weight as the determined conditions may show to be required. It is imperative that the basis of accomplishment be unequivocal here for the true estimate of these highly important, comparative effects.

Crushed material, qualified as to the shape of the crushed fragments, imposes a wider approximation and demands empyrical estimation in terms of screen sizes. The reduction coefficient, in terms of energy, is independent of the shape, so long as similarity of shape may be everywhere assumed. The averaging of dissimilar shapes, and the expression of size in terms of the screen opening, or of the observed average dimension of the pieces, is not a rough measurement, relative to the approximations that are required elsewhere in screening or classification. The calculation and consideration of size, at present, requires the assumption of some average or ideal shape. This may be the sphere, the cube, the tetrahedron, or some other definite and recognized solid form. The cube often is chosen for its simplicity but the average surface, as well as the average volume, relative to the average diameter or to the screen dimension, is a factor yet to be determined for average materials.

The work done upon the different sizes is held, therefore, as a relation rather than a dimension; the surface of a cube being assumed to give a basis of measurement upon which this proportionality may be conceived. Brunton measured the relation between the volume of the particle and the dimension of the screen opening years ago,[3] but his conclusions were harmed by the imperfectness of the screens that were then available. Departure from the shape of the cube may be cared for by the use of an equalizing factor, when known, but the study of crushing has not advanced to a point that justifies attention first to this. Qualifications as to shape are not, relatively, an obstacle to the determination of accomplishment in units. The one predominating relation is derived from the estimated total of surface within the given mass. With constants as to shape and others as to hardness, and others specific to the size, we can pronounce upon efficiency in operation, by the measurement of the size, giving the expression of the total surface. Without knowing the size, and

[3] "The Theory and Practice of Ore Sampling," *T. A. I. M. E.*, 1895, **25**, p. 835 *et seq.*

seeing that the surface is the accomplishment, we cannot go far into the useful work that requires to be done.

When, with patience, we can separate the crushed products into graded lots, and make close estimates upon the quantity of these lots, and, as accurately, determine the size, we may place some arbitrary value in energy units upon accomplishment, or surface, for given materials, crushed under known conditions. By the definition of crushing itself, the work is the production of new ruptures. The accomplishment is the extent of such ruptures shown by the surface produced. It should be clear that the part of deformation which takes the form of elastic stress is recoverable for doing work in many ways that do not require explanation here. It should be clear that the part of deformation which is plastic diminishes in extent with increasing velocity of the movement which produces the rupture, as well as with the proper direction and application of the forces. Under the influences of these compensating and power-reducing conditions the loss by deformation should approach zero, under ideal conditions, and the attainment of maximum efficiency should imply the securing of this end. As this maximum efficiency is approached, all loss diminishes inclusive of the loss by deformation. The energy expended then becomes confined to the molecules that lie contiguous to the plane of fracture. These are represented by the area of the fracture.

Much relative to efficiency we are able now to state. With hard rock the work-value is high. With tough rock the work depends greatly upon the manner of application. With a slow application of forces there is a heavy loss by plastic deformation. With fine crushing it is difficult to prevent the heavy loss by surface friction. With fissile or cleavable rock only one out of three or more necessary cuts is made easy by the qualified hardness. We can crush in such a manner as to bring out the highest resistance of deformation, developing static forces functioned into volume, or we can diminish these to a large extent. We can do any of the work of crushing in a laborious way, or in an efficient way; but the work accomplished remains the same, and is measured by the surface which is made. It would be highly desirable if we could agree upon this statement now or definitely oppose it and find reason in our belief. The development of our units of accomplishment, the growth of methods of representing the results

of practice, and the whole understanding of efficiency await this judgment.

It appears necessary to make this statement in order that none among us fall into a state of patient skepticism, awaiting a kind of demonstration that is not to be expected. From the considerations into which we have entered, it should be clear that misconception has been due to a failure to analyze the qualities of deformation. In much of the work that engineering has to do, and in the case of all the inductions of scientific theory, the reasoned fact covers the shortcomings of material demonstration, and offers the only standard of judgment that is fundamental in last analysis. It is not now so much the proof of experiment that we require as definition of what we understand that crushing means. This will give us the basis for interpreting efficiency in the work we do, and permit milling practice to pass on to the attention of more important problems.

THE Department of Terrestrial Magnetism of the Carnegie Institution has made a new analysis of the magnetic field of the earth. Of the magnetic forces manifest on the surface of the earth, 93 per cent. are due to electrical or magnetic forces within the earth, 3 per cent. to electrical systems in the atmosphere, while "the remaining portion, about 4 per cent., is apparently to be ascribed either to vertical earth currents which pass through the atmosphere into the earth and out again, or to an affect similar to the deviation of the compass needle caused by forces set in operation during the earth's rotation, or to both causes combined. . . . The earth's magnetic moment is diminishing; the annual rate of decrease during the past sixty years has been one part in 1200." G. F. S.

Effect of Pressure upon Optical Absorption. MISS F. G. WICK. (*Phys. Rev.*, March, 1923.)—These experiments carried out in the laboratory of P. W. Bridgman, showed that small effects do exist. The results are chiefly qualitative. Light from a carbon arc was transmitted through solutions and solids at normal pressure and at pressures up to 1500 atmospheres and the spectra were photographed. Generally the effect of increasing pressure was similar to that due to a lowering of temperature. In solutions increase of pressure has, in general, an effect like that caused by diluting the solution. Sometimes bands are shifted either toward the red or toward the violet or become more prominent at high pressures.

G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

A METHOD FOR THE MEASUREMENT OF SOUND INTENSITY.[1]

By J. C. Karcher.

[ABSTRACT.]

A METHOD for the measurement of sound intensity is presented which has a wide range of sensitivity, permits sound approaching the threshold value of audibility to be measured and does not necessitate the calibration of an amplifier.

The measuring instrument consists of a magneto-phone or electrostatic transmitter, and two coils whose mutual inductance can be varied by known amounts.

The e.m.f. generated by the magneto-phone due to its presence in the sound field is compared with the e.m.f. generated in one coil when the other carries a known current. The comparisons are made by successively impressing the e.m.f.'s upon an indicating instrument consisting of an amplifier, a rectifier, and galvanometer. The mutual inductance between the two coils is varied until the two e.m.f.'s are equal. The e.m.f. generated in the second coil can be computed, and since the sound intensity at the magneto-phone is proportional to the square of the e.m.f. generated, a means of making sound intensity measurements is presented.

Absolute calibration is made by comparison with a Rayleigh disc.

AERONAUTIC INSTRUMENTS.[2]

By Franklin L. Hunt.

[ABSTRACT.]

THIS paper describes various aeronautic instruments and will be useful to those interested in the general aspects of the aeronautic instrument art.[3] The instruments considered are as follows:

* Communicated by the Director.

[1] Scientific Paper, No. 473, price five cents.

[2] Technologic Paper No. 237, price twenty cents.

[3] For a more detailed discussion see Reports Nos. 125–132, inclusive, National Advisory Committee for Aeronautics, 1922.

ALTITUDE INSTRUMENTS—ALTIMETERS, BAROGRAPHS, STATOSCOPES.

Altimeters and barographs are used to indicate altitude. They are the same in principle as aneroid barometers. Changes in altitude are indicated by the expansion or contraction of one or more evacuated metal capsules which are maintained distended by springs.

Statoscopes are used in lighter-than-air craft to show small changes in altitude. Air in a heat-insulated container expands or contracts with changes of external atmospheric pressure, thereby causing liquid in a glass trap attached to the container to move and thus indicate rise or fall.

SPEED INSTRUMENTS—AIR-SPEED INDICATORS, GROUND-SPEED INDICATORS, RATE-OF-CLIMB INDICATORS.

Air-speed indicators show the speed of aircraft relative to the air. Ground-speed indicators give the speed with reference to the ground. The former depend for their action on the pressure developed in Pitot or Venturi nozzles or on pressure plates, by the motion of the airplane; or on the speed of rotation of cup anemometers or small air propellers. The nozzle pressure is measured by a sensitive pressure gage.

Ground-speed indicators depend on measuring with a stop watch the time for an object on the ground to pass between two sighting points on the ground-speed indicator or upon some rotating or reciprocating optical device which neutralizes the apparent motion of objects on the ground as seen through a telescope. Devices in which the time integral of the accelerations of the airplane are found mechanically have been proposed, but these are unsuccessful. Directional wireless telegraphy triangulation methods are also used.

Rate-of-climb indicators are like statoscopes except that the air container is connected to the external air through a fine capillary tube instead of a trap. One side of the container is a flexible diaphragm which expands and contracts under the pressure lag caused by the capillary tube, thus indicating rate of ascent and descent. Liquid manometers are also sometimes used to measure the difference in pressure between the container and the external air.

ORIENTATION INSTRUMENTS—COMPASSES, TURN INDICATORS, INCLINOMETERS.

Aircraft compasses are the same in principle as marine compasses but are much lighter in construction. They are ordinarily of quick period. To avoid the disturbing effect of masses of iron in the airplane motor distant reading compasses have been tried. One method is to use the earth's magnetic field to develop a current in a rotating coil of wire. Another uses the resistance changes of selenium cells exposed by the motion of the compass card to the light from incandescent lamps.

Turn indicators are essentially gyroscopic rotors which tend to maintain their direction in space when the airplane deviates. Rotors driven by the impact of an air stream on the serrated edge of the rotor and also those in which the rotor is the armature of an electric motor are used.

Inclinometers are either liquid bubble levels or gyroscopic rotors. The former indicate the inclination of aircraft with reference to the resultant of gravity and centrifugal force and the latter with reference to the true vertical.

ENGINE INSTRUMENTS—TACHOMETERS, PRESSURE GAGES, GASOLINE GAGES, GASOLINE FLOW INDICATORS, THERMOMETERS.

Tachometers indicate the rate of revolution of the aircraft propeller. The two types most commonly used are the centrifugal, which is the same in principle as the familiar ball governor, and the chronometric, in which the speed is measured by the amount of motion of a toothed rack or gear system in a measured interval of time determined by a clockwork escapement. Other types include magnetic tachometers in which a permanent magnet is rotated near a conducting disc, thereby dragging the disc by virtue of the eddy currents produced; electromagnetic tachometers depending on the current developed by a magneto which is connected to an indicating galvanometer; air drag or viscosity tachometer in which one disc or cylinder attached to the engine shaft rotates another disc by virtue of the viscosity of the air film between them; air pump type, consisting essentially of an air pump which forces air through a pressure indicator.

Air and oil pressure gages used to indicate the air pressure in the gasoline tank and the oil pressure of the engine lubricating system are ordinarily of the familiar Bourdon tube type.

Gasoline gages are used to measure the gasoline supply. The most common type consists of a float which rests on the surface of the gasoline and is connected to the indicating mechanism by a metal rod or flexible cord. Another type depends upon the hydrostatic pressure of the gasoline in the tank.

Gasoline flow indicators show the rate of consumption of gasoline. In one type a metal vane restrained by a coiled spring is deflected by the gasoline as it flows through the instrument. In another, gasoline is forced out through a slit in a vertical metal tube surrounded by a concentric glass tube. The height reached by the gasoline in the metal tube as it flows through the slit depends on the rate of consumption and is indicated by a small rider which moves up and down in the slit.

Thermometers are used to indicate the temperature of the radiator water and oil supply of the engine. They are either of vapor pressure or liquid filled type according as they depend upon the variation of pressure of the vapor of a volatile liquid or the expansion of a liquid with change of temperature. A bulb containing the liquid located at the point whose temperature is to be taken is connected by small metal tubing to an indicator which is ordinarily a Bourdon tube gage.

NAVIGATING INSTRUMENTS—MAPS, DEAD RECKONING INSTRUMENTS, ASTRONOMICAL INSTRUMENTS, RADIO DIRECTION FINDER.

Maps and charts are carried on long distance cross-country flights. The position of the aircraft can also be calculated from readings of the compass, air speed, ground speed and drift with reference to the ground. Where the earth is not visible astronomical methods involving the use of sextants are available. The use of radio direction finders in conjunction with radio sending stations is also being used.

SPECIAL INSTRUMENTS AND ACCESSORIES—OXYGEN INSTRUMENTS, RECORDING INSTRUMENTS, STRUT AND GAS TEMPERATURE THERMOMETERS, TIME PIECES, MANOMETERS, HYDROGEN LEAK DETECTORS.

Oxygen instruments supply artificial oxygen to aviators at high altitudes. The gas is either compressed into cylinders or carried in liquid form and delivered to the aviator through pressure regulators which automatically control the supply in accordance with the altitude.

Recording instruments are for experimental work and airplane performance tests where permanent records of altitude, air speed, rate of revolution of the engine, rate of ascent and descent, temperature and humidity are required. These instruments are the same in principle as the indicating instrument of the corresponding type previously described but are provided with recording attachments.

Strut thermometers are used on airplanes to determine the temperature of the surrounding air and gas thermometers on lighter-than-air craft to indicate the temperature of the gas in the bags. Strut thermometers are usually ordinary liquid thermometers. They may also be of the liquid filled or vapor-pressure type described above. Electric resistance thermometers are frequently used to indicate gas temperature.

A clock or watch is carried in most aircraft. Any clock which will stand the shocks of landing and vibration may be used.

Lighter-than-air craft are equipped with manometers to control the pressure of the gas in the bags. Hydrogen leak detectors are used to indicate when gas is escaping from the bags of lighter-than-air craft. One type depends upon the pressure developed in an inclosed chamber provided with a semi-permeable porcelain back by the escaping hydrogen diffusing into the chamber. The pressure is measured by the motion of a flexible metal diaphragm.

The original paper is illustrated by many photographs of the most recent types of aircraft instruments.

ARLINGTON BUILDING.[4]

By Louis J. Larson and Serge N. Petrenko.

[ABSTRACT.]

THE hollow tile and reinforced concrete floors of the Arlington Building, Washington, D. C., were loaded and the deformations measured. This was, at the time, the first test upon this type of construction in which strain-gage measurements were taken.

The floor slab was formed by rows of hollow tiles spaced four inches in each direction. The reinforcing steel was placed in

[4] Technologic Paper No. 236, price fifteen cents.

these spaces and concrete poured around it and into the open ends of the tiles.

The columns are steel H-sections surrounded by a thick casing of concrete. The beams and girders have steel I-beams encased in concrete. These beams are generally near the bottom and may be considered the tension reinforcement.

The building, intended for a hotel, was originally designed for a live load of 75 lb./ft.^{2} On account of the purchase by the government for an office building the live load was increased to 100 lb./ft.^{2} and to care for this additional load, a 2-inch layer of concrete was placed on top of the tiles. This type of construction was new in many respects and the design was considerably lighter than that recommended by the "Joint Committee on Concrete and Reinforced Concrete." For these reasons, it was desired to find the live load which could be placed on the floor panels before too high stresses were developed. It was desired, also, to secure as much information as possible on the action of the hollow tile slab.

The panels, having various ratios of length to width (from 1.05 to 1.86) were loaded with sand bags, separated by aisles to prevent arching, some up to 380 lb./ft.^{2} The loading schedule was intended to produce maximum positive and maximum negative moments and to enable the study of the effect of transferring load to an adjacent panel.

The deformation readings consisted of strain-gage measurements on the steel and concrete and deflection measurements on the slabs and on the beams. The gage lines were located at positions of maximum positive and maximum negative moment and in some panels in other places to study the distribution of bending moments throughout the panel. The deflection readings were taken at the centre of each panel and at the middle of the supporting beams. The corrections made necessary by the considerable fluctuations of temperature were based on readings on standard bars.

The maximum stresses developed in the slab were about 27,500 lb./in.^{2} in the negative reinforcement and 24,000 lb./in.^{2} in the positive reinforcement. Both stresses were developed at the load of 335 lb./ft.^{2} The stresses developed in the reinforcing

I-beams of the girders were lower. The maximum recorded compressive stress in the concrete was about 1600 lb./in.^{2}

The distribution of the cracks in the concrete furnished an indication of the distribution of the stresses at an early stage of the test. The first cracks observed were diagonal ones on the bottom of the slab. They occurred at about the same time as the cracks on the top which extended across the corners and at right angles to those on the bottom. The cracking of the concrete was accompanied by a considerable increase of the stresses in the reinforcing steel. The study of the cracks and the stresses shows that in a test of this kind, the deformations, though measured at positions of maximum moment, will fall far short of showing the maximum stresses unless the gage lines are located across, or very close to, the principal cracks. Thus, in some cases, the stresses observed at positions of maximum moment and at the gage lines crossed by cracks were 16,000 and 23,000 lb./in.^{2}, while stresses in gage lines 12 inches from the cracks were 4000 and 5000 lb./in.^{2}, respectively.

The effect of time under load was very pronounced in the first twenty hours and comparatively small later.

The effect of increasing the ratio of the length to the width of the panel was to increase the moments carried by the positive and the negative reinforcement in the short span and a corresponding decrease of the moments in the long span.

The beams offered very little resistance to torsion and the stresses in the negative reinforcement across the beam were little affected by the transfer of load across the beam.

The increase of the deformation in the reinforcement due to long-continued loading was greater than that in the concrete. This probably was partly due to the assistance of the clay tiles in resisting the compressive deformation because of the clay tiles yielding less than the concrete.

The moment coefficients are generally small due to the low stresses and are not proposed for use in design but to show the relative amount of bending moment carried in the two directions.

From the comparison of these results with those obtained from tests of simple beams, it appears that the factor of safety of the construction is apparently higher than 2.

METHODS OF MEASUREMENT OF PROPERTIES OF ELECTRICAL INSULATING MATERIALS.*

By J. H. Dellinger and J. L. Preston.

[ABSTRACT.]

THE Bureau of Standards receives frequent requests for information on the methods which it has found practicable for making measurements of properties of electrical insulating materials. The methods are described in this paper, and are the methods that were used in the research described in the previous publication by the same authors, Technologic Paper No. 216, "Properties of Electrical Insulating Materials of the Laminated, Phenol-methylene Type." The reasons for selecting certain physical properties for measurement in a research on electrical insulating materials, and the definitions of the properties are detailed in that paper. The same considerations apply in the measurement of many types of insulating materials besides the laminated phenolic materials. The properties for which methods of measurement are described are: Phase difference and dielectric constant at radio frequencies, voltage effects at radio frequencies, volume resistivity, surface resistivity, density, moisture absorption, tensile strength, transverse strength, hardness, impact strength, permanent distortion, machining qualities, thermal expansivity, and effects of chemicals.

Insulating materials are not perfect in their insulating qualities, and there is a certain amount of power absorption in them when used in a circuit in which alternating current flows. This effect is particularly important when the frequency is high, and it has been shown in fact that the power loss is the best single property that gives an indication of the suitability of an insulating material for use in high-frequency (radio) apparatus. The power loss can be expressed by a number of constants: The resistance, phase difference, phase angle, power factor, sharpness of resonance, and decrement. The simplest of these expressions for the power loss is the phase difference. It and related quantities are obtained by measurement of the frequency of the alternating current used and the resistance and capacity of a condenser made of the material to be tested. The measurement of the radio-frequency resistance is the most difficult part of this procedure.

* Scientific Paper No. 471, price fifteen cents.

Complete details of this and the other measuring methods are given in the paper. The dielectric constant is obtained as a result of the phase difference measuring procedure, supplemented by measurements of area and thickness of the sample.

The measurement of voltage effects is described for radio frequencies only, as injurious effects are caused at much lower voltages for radio frequencies than for lower frequencies. A small sample of the material is mounted in parallel with a condenser and observation is made of the voltage required to arc over a 2-cm. surface separation between metal electrodes.

Electricity leaks above the surface of an insulator as well as through its volume, and so it is necessary to determine both volume resistivity and surface resistivity. They are obtained from measurements of direct-current resistance and dimensions of sample. Atmospheric humidity affects the surface resistivity, and must be carefully controlled and measured.

Density and moisture absorption are measured by weight in air and in water. The moisture absorption is for a period of twenty-four hours.

Tensile strength is measured on a standard testing machine, using special adapters in the jaws to render the alignment of the test sample free and automatic. Modulus of elasticity (tensile) is measured by the aid of an extensometer between gage marks two inches apart.

Modulus of rupture and modulus of elasticity (transverse) are determined on a sample loaded at centre of a 10-inch span.

The Brinell and Shore scleroscope methods are used for measuring hardness.

Impact strength is obtained from the angular swing of a pendulum hammer which breaks a short slotted sample held in a vise.

Permanent distortion is measured as the permanent sag due to dead loads at the centre of a 12-inch span.

Machining qualities are not susceptible to as exact measurement as other properties. They are practical tests, based on averages obtained by two or more mechanicians following a prescribed routine to give the ease of machining, surface finish of machined samples, effect on machine tools for specimens sawed, turned, machine and die threaded, tapped, drilled, and shaped.

Thermal expansivity is measured on a specimen 30 cm. long either in oil or air. Microscopes are used to measure length changes and thermocouples to measure temperature.

The chemical effects include the effects of sulphuric acid and caustic soda. The sample is immersed for a period from two to sixty days, and the weight and hardness determined at specified intervals.

The information obtained by making this series of measurements on a given material is quite comprehensive, and should make possible the selection of the best material for a given use.

SERIES IN THE ARC SPECTRUM OF MOLYBDENUM.*

By C. C. Kiess.

[ABSTRACT.]

MANY of the strong lines of the arc spectrum of Mo have been found to be members of series. These are of several types. Narrow triplets characterized by the frequency differences 121.5 and 87.0 have been arranged into the series $1S - mP_1$, $2P_1 - mS$ and $2P_1 - mD$. Widely separated triplets, between which the frequency differences 448.5 and 257.5 exist, form the series $1s - mp_1$, $2p_1 - ms$ and $2p_1 - md_1$. Parallel to these wide triplet series are other series $1s - (mp_1 + k_1)$, $(2p_1 - k_1) - ms$ and $(2p_1 - k_1) - md_1$, of which the separations 379.9 and 233.4 are characteristic. The limits of these series have been calculated with formulas of the Ritz type and with the aid of the inter-series combination-lines $1s - 2P_2$, $1s - 2P_3$, $1S - 2p_2$, and $1S - 2p_3$. From the known values of $1s$ and $2p_1$ it follows that the resonance and ionization potentials of Mo are 3.25 volts and 7.35 volts, respectively. In addition to the triplets there occur in the spectrum of Mo, groups of 9, 10, and 13 lines known as multiplets, which arise from the combinations of the various threefold and fivefold levels which exist beyond the $1s$ level of the atom.

WOOL is produced in every State in the Union, according to reports of the United States Department of Agriculture. In 1922 production totalled 219,095,000 pounds (not including pulled wool) compared with 225,546,000 pounds in 1921. Wyoming and Texas led in production in 1922, having produced 22,500,000 pounds and 19,300,000 pounds, respectively.

*Scientific Paper No. 474.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

A SPECIAL SENSITOMETER FOR THE STUDY OF THE PHOTOGRAPHIC RECIPROCITY LAW.[1]

By L. A. Jones.

A SENSITOMETER built especially for a critical study of the failure of the reciprocity law is described. The requirements of such a sensitometer are outlined and a detailed description of how these various requirements are met is given. Exposures are given by means of a rotating sector wheel which is driven by a constant speed motor. The arrangement is such that a plate is exposed by a single turn of the sector wheel, thus eliminating the intermittency effect inherent in the usual type of sector wheel sensitometer. By means of a series of gears, it is possible to vary the angular rotational velocity of the sector wheel over a very wide range so that exposures automatically timed may be given, varying from .0002 second up to 16 hours. The required variation in the illumination incident on the photographic plate during exposure is obtained in part by the variation of the distance between the light source and the plate and in part by a variation in the effective size of source. An intensity range of about one to one million is available. The sector wheel is driven by a constant speed governed motor which can be checked directly against the beat of a seconds pendulum.

As a result of experimental work conducted near Block Island by the Subaqueous Ranging Section of the Coast Artillery Corps, it has been established that the speed of sound in salt water increases 2.8 metres per second for each Centigrade degree of increase in temperature from 0° to 20° C. The effects of change of density and salinity are included in the increase stated. They are small in comparison with the temperature effect. (*Phys. Rev.*, March, 1923.)

G. F. S.

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* Communicated by the Director.

[1] Communication No. 161 from the Research Laboratory of the Eastman Kodak Company and published in *Jour. Opt. Soc.* and *Amer. Rev. Sci. Inst.*, April, 1923, p. 305.

Increasing Rubber Output.—Oil and rubber are two of the most important world staples at the present time and struggles to obtain control of regions in which they may be obtained are disturbing the diplomatic relations of the great nations. A wonderful increase of rubber supply has resulted from the cultivated plants, just as the supply of quinine has been increased by the cultivation of the cinchona trees. Apart from the advantage of extending the area in which a given plant grows is the improvement of the strain so as to secure a greater yield or to develop individuals less subject to damage from weather conditions or enemies. The growth of the plantation rubber industry is shown by figures given in Tuttle's recent book on the "Analysis of Rubber." In 1903, 25 tons was the output of plantation rubber, but in 1919, 360,000 tons were produced. Many plants carry milky juices, technically called "latex," but only a few so far known are of commercial value. *Hevea brasiliensis* Muell. Arg., is the most important source. The issue of the *India Rubber World* for May, 1923, gives an interesting and detailed account of methods of bud-grafting for improving the yield of latex. Investigations in some plantations showed that a considerable proportion of trees yielded but little of the desired material, while other trees were fruitful. At present the average production is about 5 pounds per tree per year, but instances of as much as ten times this yield have been observed. From analogy of other plants it would seem that the grafting of buds of the high-yielding trees upon one year seedlings would insure the development of a high-grade stock, and some experiments lately undertaken in the Dutch East Indies have been sufficiently encouraging to warrant more extended work.

In the issue of the *India Rubber World* from which the above note is taken, the article is by G. E. Perry, presenting the histology of the *H. brasiliensis*, liberally illustrated. Mr. Perry, who is a graduate of the Massachusetts Agricultural College, spent several years in the rubber-producing regions. At present only a small area of bud-grafted plants is under cultivation. H. L.

Magnetic Measurements in Normandy. C. E. BRAZIER. (*Comptes Rendus*, April 3, 1923.)—All the observations were made in the two departments separated by the lower reaches of the Seine. Since 1896 the mean declination has changed by 3° and the inclination by .29°. Both these changes are diminutions, while the intensity has increased by .0014 dyne. It appears, however, that the secular variation is not uniform even over so restricted a region. Four stations on the coast, including Dieppe and Fecamp, show values distinctly less than the average, 2.57°, .25°, and .0006 dyne. "This fact, which seems not to proceed from errors of observation, suggests the idea that the displacement of isomagnetic lines must be accompanied by changes in their form quite small, yet appreciable at the end of a score of years." G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

FURFURAL FROM CORNCOBS.[1]

I—FACTORS INFLUENCING THE FURFURAL YIELD IN THE STEAM-DIGESTION PROCESS.

By F. B. LaForge.

[ABSTRACT.]

THE reactions involved in the production of furfural from corncobs by the steam-digestion process occur in three stages. The conversion of the pentosans into furfural does not take place quantitatively; the yield depends upon the temperature, the time, and the ratio of the amount of cobs to the amount of water employed. The optimum conditions of operation were determined in order to apply them to larger-scale investigations. These conditions are a temperature of about 180° C., a reaction period of about two hours, and a ratio of cobs to water of not greater than 1 : 4.

CATALYTIC OXIDATION OF ANTHRACENE TO ANTHRAQUINONE.[2]

By C. E. Senseman and O. A. Nelson.

[ABSTRACT.]

A CATALYTIC method for the preparation of anthraquinone, an important intermediate in the manufacture of dyes, has been patented by Gibbs and Conover, and worked out in the Bureau of Chemistry.

The apparatus consists essentially of a carburettor, a reaction chamber, and a sublimer, all made of glass and heated by well-insulated electric heaters. The carburettor is built with two air inlets—one arranged so that the air will sweep over the molten anthracene, thus carrying a definite quantity of the hydrocarbon into the reaction chamber, the other arranged so as not to interfere with the work of the first, but to vary the air-anthracene concentration as desired.

The catalyst, vanadium pentoxide, may be supported (1) by

* Communicated by the Chief of the Bureau.

[1] Published in *J. Ind. Eng. Chem.*, **15** (May, 1923) : 499.

[2] Published in *J. Ind. Eng. Chem.*, **15** (May, 1923) : 521.

boats, (2) by discs, (3) by pumice, or (4) by fusing to a glass tube.

The sublimer, as used during most of the runs, consists of a Kjeldahl flask with neck removed, jointed to the reaction chamber by a ground-glass joint.

The maximum yield obtained was 81.2 per cent. of the theoretical.

On a New Method for the Generation of Sound-waves. JUL. HARTMANN, Copenhagen. (*Phys. Rev.*, Dec., 1922.)—"If air is allowed to stream from a container in which the absolute pressure is more than 1.9 atm.—that is, the over-pressure is higher than 0.9 atm.—through a hole or a short bore out into the free atmosphere, a jet is produced which exhibits a peculiar periodic structure. . . . It is now known that the periodical structure is closely connected with the fact of the velocity of the jet, with sufficiently high over-pressure, being higher than that of the sound." A study of the jet made with a Pitot pressure gauge shows that the pressure rises and falls as we move outward along the stream of air. There are thus portions of the jet where the pressure increases at the same time with the distance from the orifice. If the fine aperture of a bulb containing air be introduced into one of these intervals of instability, air will alternately flow into and out of the bulb and a tone is produced. Such air waves are, however, of less value than those obtained by inserting the mouth of a plain cylindrical resonator into an interval of instability. The wave thus produced has a length equal to about four times the length of the resonator. "It (the intensity) is ordinarily very high, due undoubtedly partly to the high density of the energy in the air-jet, partly to a comparatively very high efficiency of the generator. (Provisory measurements seem to prove that the efficiency at about 20,000 periods per sec. is as high as 10 per cent.) As to the frequency, resonance-oscillations, *i.e.*, pure acoustic oscillations of 100,000 periods or more, can easily be produced by means of a jet of atmospheric air. With a jet of hydrogen a frequency of more than 300,000 can be obtained. As a matter of fact the author has been able to produce intense sound-waves of 340,000 periods, and in all probability there will be nothing to prevent the production of still higher frequencies. The author therefore holds the opinion that the air-jet in connection with a resonator furnishes a means for producing intensive, pure acoustic oscillations of higher frequencies than has hitherto been possible." The structure of the apparatus is shown and it is not complicated.

"With a resonator of about 10,000 periods per sec. the produced tone was with even rather small over-pressures almost unbearably intensive and left the observer with a physiological after-effect of several hours' duration." G. F. S.

NOTES FROM THE U. S. BUREAU OF MINES.*

THE METALLURGICAL TREATMENT OF ZINC RETORT RESIDUES.

By B. M. O'Hara.

THE residues resulting from the retort distillation of zinc ores have from 40 to 75 per cent. of the weight of the original ore and contain from 5 to 15 per cent. zinc. A rough estimate indicates that approximately 450,000 tons of residue are produced annually in the United States, containing about 36,000 tons of zinc. Besides the current production of residues there are at many smelter sites large accumulations from past operations which are available for treatment if this can be done profitably. In addition to their zinc content the residues contain much unconsumed coal, which has been carbonized during the distillation process, and those from most western ores also contain lead and silver.

A survey was recently made by the Bureau of Mines, in coöperation with the Missouri School of Mines and Metallurgy, of processes which are in use or which have been suggested for the treatment of retort residues.

These methods may be classified as follows:

(1) Smelting directly in the lead blast furnace for the recovery of lead, copper, and precious metals.
   a. Residues mixed in small proportions with ore charge.
   b. Residues smelted alone with the necessary fluxes.
(2) Burning and sintering to remove carbon and furnish a desirable product for the lead blast furnace, followed by blast furnace smelting.
(3) Dry screening.
   a. For the recovery of coke.
   b. For the concentration of lead and precious metals into an enriched product.
(4) Magnetic separation.
(5) Wet concentration.
   a. For the recovery of lead and precious metals only.
   b. For the recovery of zinc and coke.

* Communicated by H. Foster Bain, Director, Bureau of Mines.

(6) Burning on Wetherill grates for the production of zinc oxide.

(7) Miscellaneous.

Most of these methods are, or have been, in actual use in one or more zinc smelters. Different methods are suited to different conditions; some have been successful in certain plants and unsuccessful in others.

It is probable that conditions are such at some plants that the retort residues cannot be profitably treated by any method; on the other hand, it is probable that many companies which do not now treat their residues could do so, if the proper method were chosen, and properly adapted to the particular conditions existing.

The treatment of old condensers is simpler than that of retort residues, and it seems that most zinc smelters could with profit build at least a simple jigging plant for their concentration. Further details will be found in Serial 2475, which was read at the meeting of the American Zinc Institute, May 7 and 8, 1923.

FLUORSPAR MINING IN THE WESTERN STATES.

By Raymond B. Ladoo.

IN order to obtain comprehensive and authentic information on fluorspar mining in the western states, the writer, together with and at the request of representatives of some of the largest fluorspar producers of the Illinois-Kentucky district, spent the month of April, 1922, in examining all western fluorspar deposits (of which record was available) believed to be of possible commercial importance.

After weighing all evidence by actual examinations and by available information from other sources, the following conclusions were reached:

(1) With one exception, all of the deposits worked have been so small, or so far from transportation, or contain fluorspar so mixed with silica or barite or both, that profitable production of *gravel grade* of fluorspar, acceptable to eastern steel mills under present standards, has been impossible, and the future seems no more promising. There are two small mines which would yield a few hundred tons annually by screening hand-picked ore, but from present indications, these properties do not justify the erection of mills.

(2) With only one exception, the most accessible ore from the mines which have been worked has been removed. The mines are, for the most part, in poor physical condition, and future operations will be increasingly difficult and expensive.

(3) Most of the western mines have long and expensive hauls to railroad, and the ore bodies are too small to justify the cost of installing improved methods of transportation, or modern mining and milling equipment.

(4) The production of *acid fluorspar* west of the Mississippi River from ore bodies now known probably will not exceed 100 tons annually. It is believed that not over 3000 tons of *ground fluorspar* can be annually produced, of which one-third will be low grade.

It was estimated that the properties visited in the western states can produce for a few years a maximum of 13,000 tons annually of a grade of *gravel* analyzing on an average 5 per cent. or higher in barite, and a maximum of 4000 tons of *fluxing lump*. The western steel mills, on account of the difficulty of obtaining fluorspar in gravel form, have been accustomed to use in their open-hearth furnaces both lump and gravel. The estimated consumption of the western mills is 10,000 tons annually, and they will probably continue to utilize western fluorspar on account of the high freight rates applicable to the Illinois-Kentucky product.

The foregoing estimates of production represent the theoretical possibilities of the western mines, which it is not believed will be reached in practice. Further details will be found in Serial 2480, recently issued by the bureau.

LUBRICATING OILS FROM PACIFIC COAST PETROLEUM.

By Earl C. Lane and N. F. LeJeune.

CALIFORNIA crudes differ in many characteristics from the petroleum produced in other parts of the United States, and the claim has been made that some of the present Federal specifications for petroleum products tend to discriminate against California products. The bureau is making a survey to determine what particular specification requirements California petroleum products characteristically fail to meet, how widely the products deviate from these requirements, and if possible to show whether the fault lies with the specifications or the products, or along what

lines investigation to determine the question should proceed. The properties of gasoline and mineral spirits made from California crudes are described in Serial 2342.

The next group investigated was lubricating oils. Sixty-one samples of lubricating stocks and finished commercial products were generously donated by four of the large refining companies of California. Fifteen samples of automobile lubricating oils, made in California from California crudes, were purchased in the open market. Nine samples of lubricating oils made from gulf coast crude were contributed for comparison by a company in Texas.

Most of the oils meet the specification requirements as regards flash point, viscosity, pour point, corrosion and reaction tests, except for deviations which for the most part are of minor importance.

Of the 78 samples of California oils tested, 90 per cent. failed to meet the requirements of the emulsion and demulsibility tests. It is recognized that emulsion tests have not yet been satisfactorily standardized and possibly in a commercial laboratory some of the samples would have been passed as complying with these requirements. In this work, results of emulsion and demulsibility tests were rigidly interpreted. Also, the organic acidity of many of the samples is above the limit permitted by the specifications. It has been suggested that failure to pass emulsion and acidity requirements may have been caused by contamination with soldering flux from the containers. This hardly seems possible, as the gulf coast samples were much more resistant to emulsification and low in acidity although they were stored in the same kind of cans.

Lubricating oils made from California crudes are being used for many purposes with good satisfaction, and it may be that present requirements as regards organic acidity, emulsion and demulsibility discriminate against them. For certain other oils, however, these tests have been found of advantage, and it seems that the relation between these and other tests and service performance will require careful investigation before the problem can be solved.

Attention is called to the fact that the Federal specifications have been changed since these oils were manufactured and furthermore that the products described in this paper were made for sale in the open market and were not specially prepared to meet

the specifications that were in effect at the time. The close agreement between these oils and the Federal specifications indicates therefore the carefulness and skill in refining possessed by the Pacific Coast refiners.

Detailed tables showing the properties of each sample treated will be found in Serial 2482, recently published.

A New Theory of Vision. FRITZ SCHANZ. (*Zeit. f. Physik.*, Dec. 9, 1922.)—Helmholtz's theory of vision requires three fundamental color sensations and no corresponding nerves have been found. On the other hand, Hering's theory predicates three substances that are modified by the action of light and the presence of these in the eye has not been confirmed. "However long the conflict has lasted, however passionately it has been waged, neither of these theories has been able to establish itself." Leaving these elder theories in their position of stalemate the author frames a new explanation based on the Hallwachs Effect that certain illuminated substances emit electrons. He finds by experiment that solutions of albumin do this.

The light entering the eye is absorbed by the pigment of the retina and electrons are ejected. Their velocity depends on the wave-length of the light to the absorption of which they owe their emission. These electrons, impinging on the rods and cones of the eye, produce an electric current that is led away by the optic nerve. An interesting parallelism, experimentally established between the action in the eye and the Hallwachs Effect, lies in this, that, when monochromatic light falls on the eye, the nerve current that appears is characteristic of the wave-length of the light and that its original strength grows greater the shorter the wave-length is made. Just the same relation between wave-length and the photoelectric current strength has been found by Ladenburg to hold for metals on which light falls.

How can Schanz's theory account for color vision? Let pure spectral monochromatic light fall on the eye. It is absorbed and electrons of a certain velocity are emitted. These are caught on the rods and cones, a current of a strength corresponding to the velocity is developed, and this current is translated into a perception of a color. But the eye cannot distinguish between a sensation due to monochromatic light and one caused by the simultaneous action of two or more lights of properly selected wave-lengths. The explanation of this is not convincing. Suppose two different wave-lengths of light fall on the eye at the same time. Each causes the emission of electrons of a certain velocity. These electrified particles travel side by side and mutually influence the velocity of their neighbors, with the result that they finally all assume the same velocity and produce the same current and ultimately the same sensation of color as if they had all been emitted with the velocity to which they all finally attained.

G. F. S.

West African Palm Oil.—The production of palm oil in West Africa has hitherto been limited almost exclusively to wild trees, and the methods have been inefficient, resulting in a lower yield and a poorer quality than can be obtained by proper means. In recent years a careful study of the subject has been undertaken in the Dutch West Indies, and the development there threatens the British industry, and it will be advisable for British interests to investigate the situation in their own region and also to examine as to whether the palm may not be cultivated in other tropical areas under British control.

The threat of the Dutch competition is along three lines. First, scientific cultivation produces a far greater yield of oil; second, modern labor-saving appliances reduce the cost of obtaining the oil; and third, the introduction of organized plantation administration with central factories gives great advantages in meeting the market demands. Machinery for the extraction and treatment of palm oil is not of recent invention. Over forty years ago a machine for cracking the nuts and for other purposes was invented, but failed to get acceptance. At present considerable machinery is in use, but definite description of much of it is not available. A bulletin recently issued from the U. S. Department of Commerce gives in considerable detail the nature and operation of the machines recently devised for obtaining palm oil. Palms, as a class, are numerous and include many very useful plants. Their imposing appearance and uses have attracted the admiration of human beings through many centuries. Oils, waxes, fibres, fruits and vegetable ivory enter in commerce in large volume. The West African palm is confined to tropical Africa. The annual export of the oil is estimated at 530,000 tons. In favorable districts, the trees occur in dense forests. Two kinds of oil are obtained from different parts of the fruit. The natives use the oil regularly as an addition to food. H. L.

IN Bohr's atom of hydrogen, radiation is emitted when an electron displaces itself from one stable orbit to another and the wave-length of the radiation depends upon the location within the atom of the two orbits. When the electron goes from the third to the second orbit the wave-length of the emitted light is 656$\mu\mu$, while 486$\mu\mu$ and 434$\mu\mu$ are the lengths of the waves sent out when the electron goes from the fourth and the fifth orbits, respectively, to the second. From a study of the intensities of these three lines as produced in a Geisler tube the author, who is the director of the Physical Institute of Moscow, has been able to calculate that the number of electrons springing over from the fourth orbit to the second is 25 per cent. of the number passing from the third to the second and that the number going from the fifth to the second is only 17 per cent. of those transferring themselves from the third to the second. "Thus the quantity of springing electrons decreases with the increasing of the distance of the electrons from the centre." G. F. S.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, June 6, 1923.)

HALL OF THE INSTITUTE,
PHILADELPHIA, June 6, 1923.

MR. W. H. FULWEILER *in the Chair.*

The following reports were presented for final action:

No. 2803: Kingsbury Thrust Bearing. Elliott Cresson Medal to Albert Kingsbury, Esq., of Philadelphia, Pennsylvania.

No. 2812: Surface Tension Apparatus. Certificate of Merit to Dr. P. Lecomte du Noüy, of New York City, New York.

R. B. OWENS, *Secretary.*

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, June 13, 1923.)

RESIDENT MEMBERSHIP.

ALEXANDER BROWN COXE, ESQ., Agriculturist, Paoli, Pennsylvania.

MRS. SELINA EMMA PEACOCK, Organist, 1919 Master Street, Philadelphia, Pennsylvania.

FREDERICK M. ROONEY, ESQ., General Manager, Hiergesell Brothers, 2011 Bellevue Avenue, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERSHIP.

W. G. H. FINCH, ESQ., Radio Editor and Engineer, International News Service, New York City, New York.

DR. ARCHIE DAYTON POWER, Physicist, University of Minnesota, Minneapolis, Minnesota.

RICHARD H. RANGER, ESQ., Radio Engineer, 66 Broad Street, New York City, New York.

DR. WILLIAM WILSON, Engineer, American Telephone and Telegraph Company, 195 Broadway, New York City, New York.

CHANGES OF ADDRESS.

MR. C. E. SARGENT, Greenfield, Illinois.

DR. FANNY R. M. HITCHCOCK, 37 Maple Avenue, Warwick, New York.

NECROLOGY.

Charles N. Butler, Esq., 1318 Land Title Building, Philadelphia, Pennsylvania.

Dr. Rudolph Hering, 1 West Seventieth Street, New York City, New York.

Mr. Alfred Mellor, 152 West Walnut Lane, Philadelphia, Pennsylvania.

Mr. F. H. Rosengarten, 1905 Walnut Street, Philadelphia, Pennsylvania.

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BOOK REVIEWS.

LAW CHARTS AND PATENT ENGINEERING. By Harry H. Semmes and Harry R. Van Deventer. 358 pages, 24 charts, 8vo. Washington, D. C., Semmes and Semmes, 1922. Price, $10.

The authors describe this work as "the first attempt" to present in graphic form the functioning of an engineer attorney, and the procedure before the United States Patent Office and the Federal Courts. The book is thus addressed to that somewhat hybrid profession which combines the functions of the engineer and the lawyer. Dealing, as it does, with procedural rather than substantive matters, it is not believed that it will be of great interest to either of these professions as such. Within the limited class to which it is addressed, the older practitioners will derive little assistance from a work of so general and elementary a character. But to those who are entering upon the profession and to those who contemplate its entry the book will be of very real value. The charts of procedure as elaborated by the text give a compact, integrated view of a subject, the details of which are imbedded in formal rules of practice and other less available sources. That the book has met a very real need for this group is evidenced by the cordial reception given it by the Washington law schools which give special courses in patent law. In several of these institutions the book under review has been adopted as a text on patent procedure.

The vice which this book shares with all manuals, and which its conspicuous merit tends to accentuate, is that it gives an unreal simplicity to its subject. This danger of over-simplification is particularly to be guarded against in books addressed to the novitiates of what may be designated as a dual profession. It suggests to the lawyer a too easy assumption of the functions of an engineer and to the engineer of the attorney's rôle.

Considering more specifically the contents of the book, it will be noted that its subject-matter is broadly divisible into two parts:

1. The scope of engineer attorney's investigations into the originality, patentability and merit of the idea presented to him, and the validity and infringement of patents.

2. The procedure for securing patent protection, *i.e.*, the preparation and prosecution of an application for patent, and the procedure in the Federal Courts for the protection of the right thus secured.

The subject-matter of the first part is not to be found in any work with which the reviewer is familiar and knowledge of it is acquired, as a rule, only in the offices of practitioners. It may be remarked that the present treatment of the subject reflects the viewpoint of the patent department of a great manufacturing concern rather than that of the patent attorney in general practice. The investigations detailed are a little more elaborate than are usually feasible unless relatively large interests are involved and the client can finance extensive researches.

The patent office and court practice charted in the second part of the book finds its source largely in the rules of practice of the patent office in the Federal Equity Rules. These charts are supplemented by forms of pleading carefully selected to illustrate the various procedural steps outlined in the charts.

The only substantive law contained in the volume is an analysis of the relative rights of the employer and the employee in the inventions of the latter made in the course of his employment. This appears in the present volume as an elaborate digression and is unfortunately colored by an apparent bias in favor of the employer.

The outstanding feature of the book is the remarkable clarity and brevity it achieves by the somewhat novel use of charts.

KENNARD N. WARE.

GLUE AND GELATIN. By Jerome Alexander. 8vo, 229 pages, and index. New York, The Chemical Catalog Company. Price, $3 net.

This is one of the now well-known and much esteemed "Monograph Series" of the American Chemical Society and in form and style agrees with the previous issues. The chemistry and physics of gelatin are complicated problems and are important on account of great industries into which the material enters. Some of the important features of the problems were discussed in this JOURNAL (1922, **194**, 564) in connection with Bogue's more extended treatise, and it will not be necessary to repeat them here. Mr. Alexander is an authority in this field and his book will at once take rank as a useful manual. It is of much smaller compass than Bogue's book, but contains a large amount of information on the subject. In the introductory chapter attention is called to the error that is carried through our dictionaries in stating that horns and

hoofs yield gelatin. These portions of the animal yield keratin. Gelatin is obtained from skin and bones. Glue is simply an impure commercial form of gelatin. A frontispiece shows a copy of an Egyptian carving which has been understood as showing the use of glue for joining wood. This picture was also given in Bogue's book with the same explanation, but a note in the present work states that another interpretation of the picture has been made, namely, that the procedure is painting. Alexander does not agree with this view, but the dispute shows how misinterpretations of ancient records may be made.

The book in hand is a compact and comprehensive review of an important subject. HENRY LEFFMANN.

PLANT PHYSIOLOGY. By Vladimir I. Palladin, University of Petrograd. Authorized English edition based on the German translation of sixth Russian edition with consultation of the seventh (1914) Russian. Edited by Burton Edward Livingston, Ph.D., Johns Hopkins University. Second American edition, with biographic note and chapter summaries by the editor. xxxiii–339 pages, index and 173 illustrations, 8vo. Philadelphia, P. Blakiston's Son and Company. Price, $4 net.

The problems of plant physiology have been under investigation for many years. They are probably less difficult than those of animal physiology, but as to the fundamental phenomena the basic procedures in both fields are still unknown. What life is, is not yet determined. The tendency for many years has been towards regarding vital action as the operation of the ordinary forces of nature, but many phenomena remain to be explained, and some scientists are still adherents of the theory that vitality is a specific influence. Meanwhile, the great efforts of scientists are directed wisely to collecting facts.

It has for some time seemed desirable to bring the study of plant and animal physiology into one group under the general term "Biology," but this has not been accomplished, and workers in the two fields remain practically indifferent to each other's labors. The work before us is a very comprehensive and detailed statement of the phenomena of plant life in all its bearings. Written in Russian, it would have been of little use to the greater portion of the scientific world, so it is fortunate that it was early printed in German and still better that it has been put into English. Scientists have long been obliged to make themselves tolerably familiar with two languages besides their own, English, French and German having been dominant in scientific literature. Italian has been coming into importance, but it is to be hoped that no condition will arise that will make the acquirement of Slavic tongues necessary to a fair knowledge of current progress.

An editorial note to a brief biography of Professor Palladin, states that the text thereof is taken from the ninth Russian edition, but in the preparation of translation the seventh edition, issued in 1914, was used. A work that has gone through so many revisions may be assumed to have been brought to a highly accurate and comprehensive condition, and an examination shows this to be the case. Yet the editor, who has done his work with great care and attention, has found numerous occasions to amend or even criticize unfavorably the original statements. Scientists who devote themselves for many years to

a narrow specialty are apt to form dogmatic opinions and to propagate them in their writings. Very often the individual ignores the progress of discovery along certain lines, and thus fails to appreciate the error of interpretation and misleads those whom he teaches and for whom he writes. An interesting instance of the blocking of correct teaching is afforded in the case of the respiration of plants. In the middle years of the nineteenth century, the usual teaching was that plants take in carbon dioxide and emit oxygen, reversing the cycle that occurs in animals. Much moralizing was given to this fact as a teleologic relation, it being pointed out that in this way the plant world balanced the animal world and kept the conditions of the air uniform. Yet Boussingault had shown long before that this exchange takes place only in the light, and it was also known that a true respiration similar to that of animals is always occurring in the growing plant. The decomposition of carbon dioxide and elimination of oxygen are more analogous to feeding than to respiration. It has always been an interesting question as to what is the series of chemical changes following the decomposition of carbon dioxide. Baeyer suggested in 1870 that formaldehyde is the first product. A simple equation can be shown by which this substance is formed from carbon dioxide and water, with elimination of oxygen. By polymerization, starch can be obtained without taking up or losing an atom. That starch production is a common process in plants under the influence of light has been well established. Starch by a simple hydrolysis will yield one of the hexoses, which are freely soluble in water, and thus may be rapidly transmitted through the plant cells. It seems that the primary formation of starch is necessary as a storage form, since the soluble sugars would be liable to fermentations. It is, of course, well known that many plants store large quantities of starch, and that these collections are usually associated with one or more catalysts that have the power to accelerate hydrolysis when the vegetable structure is in favorable conditions of heat and moisture. Simple and attractive as the theory of formaldehyde formation and polymerization is, there does not appear to be absolute proof of its truth.

Some considerable changes may be expected soon in the aspects of plant physiology. The importance of the hydrogen-ion concentration has already been emphasized, and it seems likely that a very large part of extensive and laborious work that has been done on soil analysis and the effects of fertilizers will have to be put on the scrap-heap when the data as the hydrogen-ion concentrations of soils have been accumulated in quantity. The problems of plant ecology also open a wide field of investigation. Conditions of association, epiphytism, symbiosis and partial and complete parasitism are widely distributed. Parasitism itself offers an interesting and difficult field extending from the limited relations of species of *Scrophulariaceæ*, *Loranthaceæ* and *Santalaceæ*, through the almost complete dependence of the genus *Cuscuta*, to the banditry of the *Orobanchaceæ*.

The translation is very well done, showing no evidence of either the German or Russian idiom. As Doctor Livingston remarks, western Europe and America have seen Russian literature principally through German or French, and such intermediaries are liable to mislead. It is necessary, therefore, in important matters to go back to the original, which the editor of this book has done. The transliteration of Russian names is one of the difficulties

in dealing with such translations, and, unfortunately, translators do not agree on some of the points. The name of the author of the book is often given as W. Palladin, but it should be V. Palladin, the accent is on the penultimate syllable and no final "e" should be used. A statement of the principles followed with regard to Russian proper names is given in detail.

The book is filled with most interesting biologic information. The literature has been searched with great thoroughness and care and an extensive bibliography is given in the form of footnotes. The editor inclines to some simplification of spelling, but is unfortunately restrained by the conventions in the matter. His scholarship is shown by his calling attention to the fact that "enzyme" should be pronounced with the accent on the first syllable, and he properly observes that the spelling should be without the final "e." He has done well in the matter of bibliographic references, though the reviewer does not like one method adopted. The series number is given in Roman numerals (expressed in Italic capitals), but it would be better to use the now fairly common method of Arabic numerals in brackets, [3], instead of *III*. Efforts should be made to get rid of the Roman numerals. Doctor Livingston has made the proper step in using full-faced Arabic type for the volume number, and it is to be regretted that he did not carry the reform further. It is true that as the series numbers are low, the complexity of the Roman numerals is not in evidence, but in reforming this absurd practice, it would be better to reform it altogether. The mechanical execution of the book is excellent and it constitutes a valuable up-to-date contribution to biology.

HENRY LEFFMANN.

BIBLIOGRAPHICAL HISTORY OF ELECTRICITY AND MAGNETISM, chronologically arranged. Compiled by Paul Fleury Mottelay, Ph.D., with an introduction by the late Sylvanus P. Thompson, D.Sc., F.R.S., and a foreword by Sir R. T. Glazebrook, K.C.B., D.Sc., F.R.S. 8vo, xix–564 pages, frontispiece and plates. Philadelphia, J. B. Lippincott Company, 1922.

This monumental work represents many years of patient, laborious searching of records, musty and recent. The author and the writer of the introduction have both closed their earthly careers, but the book will remain a testimony to their services. The author, of course, deserves by far the greater honor, for the introduction is brief and merely a summary of interesting points. The main portion of the text of the book has appeared in periodical literature, *viz., Engineering, The Electrical World, La Lumière Électrique* and *L'Industrie Moderne*, respectively, London, New York, Paris and Brussels. In preparation for this book, the texts of these articles have been carefully revised both as to recorded data and literary form, and many new entries added. In addition to the recording of inventions and discoveries, biographical information has been added concerning many of the more prominent workers in the field covered by the book.

Knowledge of some phenomena of electrical action goes back to a remote past. It has long been known that Greek philosophers were familiar with the property of amber acquiring attractive powers by friction, and properties of the lodestone were also noticed at a very early time. When one searches for the initiator of any invention or discovery, it will generally be found that the task is

difficult and it is often impossible to fix the first step definitely. Much careful weighing of evidence and much searching of out-of-the-way tomes are required. The present work is interesting as showing the early date at which the phenomenon of magnetism was apparently known and employed. The date is B.C. 2637, for which several references are given. The item is from Chinese records, and describes the employment of a figure which had the power to point always to the south, so that the army of Hoang-ti was able to pursue an insurgent band through a fog. Notwithstanding the eminent writers from whom this account is quoted, implicit acceptance of such records is hardly advisable, and the date is given without any indication of its possible error. In Greek, Babylonian, Jewish and Egyptian history, dates are very uncertain, and it is scarcely proper that Chinese records going back so far should be accepted without hesitation.

The book is not a history; it is not even a readable volume. It is as unsatisfactory as a dictionary. As a source of material for a comprehensive and valuable history of electricity and magnetism, it will be most valuable, and it is to be hoped that its publication will induce some one to undertake such a history. That work must be done in a critical spirit. The philosophy of history as now in vogue must be applied. It is true that the vast mass of the work done by the workers in this field was without money and without price, so the economic influences which bulk so largely in most human labors do not play a large part here, still it is the duty of the historian to search and set forth the underlying motives in all developments.

Striking, interesting and well-executed plates are included in the volume, and the mechanical character is good with one exception. The binding is much too close, not enough margin being left on the inside of the page. This makes the book difficult to read as it has to be held open with some force. Another fault is the method adopted in the index. This is very full and elaborate, but no indication is given as to the pages on which the more important data concerning a given subject are to be found. In extensive indexes of this character, some pages should be indicated by distinct type so as to facilitate reference to the principal discussion of the subject. The work is a valuable contribution to the literature of the subject.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 157, Nomenclature of Aeronautics. 59 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This "Nomenclature for Aeronautics" was prepared by a special conference on aeronautical nomenclature of which Dr. Joseph S. Ames was chairman. The conference was authorized by resolution of the executive committee of the National Advisory Committee for Aeronautics on January 26, 1922, and the committee officially invited the Chief of the Army Air Service, the Chief of the Bureau of Aeronautics of the Navy Department, the Director of the Bureau of Standards, the Second Assistant Postmaster-General, the Society of Automotive Engineers, the American Society of Mechanical Engineers, and the Aeronautical Chamber of Commerce to designate representatives to serve

on the conference on aeronautical nomenclature. This report supercedes all previous publications of the committee on this subject. It is published with the intention of securing greater uniformity and accuracy in official documents of the government and insofar as possible in technical and commercial publications.

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Principles of Chemical Engineering, by William H. Walker, Warren K. Lewis and William H. McAdams, Professors of Chemical Engineering at the Massachusetts Institute of Technology. 637 pages, illustrations, folded diagram, 8vo. New York, McGraw-Hill Book Company, Inc., 1923. Price, $5.

The Nebular Hypothesis and Modern Cosmogony, being the Halley Lecture delivered on May 23, 1922, by J. H. Jeans. 31 pages, plates, 8vo. New York, Oxford University Press, American Branch, 1923. Price, 85 cents.

Éléments de la Théorie Électromagnétique de la Lumière, par Ludwig Silberstein, ancien professeur de Physique mathématique à l'Université de Rome. Traduit de l'Anglais par Georges Matisse. 93 pages, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, 6 Francs.

Essentials of Drafting, by Carl L. Svenson. Second edition, revised. 194 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1923. Price, $1.75.

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J. B. LIPPINCOTT COMPANY
PHILADELPHIA